OBSERVATIONS ON THE IRON-NITROGEN SYSTEM

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ABSTRACT

By means of thermal analyses, microscopic examinations, and X-ray analyses of nitrided electrolytic iron specimens a study has been made of the iron-nitrogen system. From the data obtained and with the diagrams of Sawyer and Fry as a basis, a modified iron-nitrogen constitution diagram has been tentatively drawn. The upper temperature horizontal noted by Sawyer was also observed, but this has been ascribed to a peritectoid instead of a eutectoid transformation. Three nitrided layers were observed, whereas Fry noted only two. The three layers have been designated as Fe_2N, Fe_4N, and Fe_6N. Observations on several specimens of aluminum molybdenum nitriding steel are also described.

CONTENTS

I. INTRODUCTION

From the standpoint of nitriding, the constitution diagram of the iron-nitrogen system is important, mainly because it must form the basis of our understanding of the more complex system involved in the nitriding of the special alloy steels. No practical use has been made, or is very likely to be made, of nitrided pure iron. The iron-nitrogen system may conveniently be divided into two parts—one of a low nitrogen content corresponding with the core of nitrided articles and one of a much higher nitrogen content, corresponding with the case.

The low-nitrogen side of the diagram is of general importance, since it is believed that comparatively small amounts of nitrogen may materially affect the mechanical properties of iron and steel. According to the diagram as determined by Fry,[1] the iron-nitride constituent, familiar to metallographers in its characteristic needle form, is appreciably soluble in iron in the temperature range 500° to 550° C. and much less soluble at room temperature. This suggested to Griffiths[2] that nitrogen may be a factor in the temper brittleness of steel and he obtained evidence tending to support this view. More recently, Dean, Day, and Gregg[3] showed, as was predicated by

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[1] Fry, A., Stickstoff in Eisen, Stahl und Sonderstahl. Stahl und Eisen, **43**, p. 1271, 1923; Kruppsche Monatshefte, **4**, p. 138; 1923.
[2] Griffiths, W. T., Note on Nitrogen as Possible Factor in Temper Brittleness, J. Iron & Steel Inst., **111**, p. 257; 1925.
[3] Dean, R. S., Day, R. O., and Gregg, J. L., Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-Nitrogen, Technical Publication No. 193, A. I. M. M. E.; 1929.

Sawyer,[4] that the needlelike iron-nitride constituent causes precipitation or dispersion hardening in iron and therefore likewise suggested that temper brittleness and blue-heat phenomena in iron may be due to nitrogen. An investigation of the iron-nitrogen system by Murakami and his associates has been announced,[5] in which two compounds on the iron side of the diagram have been found by means of magnetic analysis and microscopic examination. Only the results of the X-ray studies were available in published form at the time the bureau report was written.

The accurate determination of the iron-nitrogen diagram, especially for alloys of high nitrogen content, is extremely difficult. Fairly homogeneous alloys of iron and nitrogen of very low nitrogen content can be obtained by melting iron in an atmosphere of nitrogen, but alloys of high nitrogen content can not be produced in this way, even under very high pressures of nitrogen. Under a pressure of 3 atmospheres Sawyer [6] obtained an alloy of 0.034 per cent [7] nitrogen content, under 200 atmospheres Andrew [8] obtained an alloy of 0.3 per cent nitrogen, and according to a calculation by Sawyer under 900 atmospheres an alloy of 0.6 per cent should be obtained. According to Sawyer's calculation, the constant, 0.02, multiplied by the square root of the nitrogen pressure gives the percentage of nitrogen in the alloy. Since the nitrogen pressure enters into this formula as the square root it will be apparent, that, if even the formula is approximately correct, obtaining very high nitrogen content in iron by melting under pressure is hardly practicable.

The usual method of introducing nitrogen into iron is by diffusion into hot solid iron; molecular nitrogen does not diffuse appreciably, and nascent nitrogen, such as is formed by "cracking" ammonia gas by passing it over hot iron, is necessary. In this way iron-nitrogen alloys containing a maximum of about 11 per cent nitrogen may be produced. However, the nitriding is not uniform, but takes place by the formation of several distinct layers of different iron-nitrogen compounds and constituents, so that the chemical composition of even a very small nitrided particle may vary discontinuously from a small fraction of a per cent near the center to the maximum of about 11 per cent nitrogen at the surface. The difficulty of determining and interpreting critical points in such specimens by a precise method, such as thermal analysis, is manifest. Moreover, there is the added difficulty that the nitride layers are very unstable, nitrogen gas being liberated upon heating to temperatures as low as 300° C. and the gas evolution increasing rapidly at higher temperatures. Thus, during a thermal analysis the chemical composition of the specimen is always changing, and the heat effects produced by the gas evolution may obscure transformation points or be mistaken for them. The fact that the iron-nitrogen alloys decompose when heated makes it practically impossible to obtain homogeneous specimens by annealing, except with those of comparatively low nitrogen content. The

[4] Sawyer, C. B., Nitrogen in Steel. Trans. Am. Inst. Min. & Met. Eng. **49**, p. 799; 1923. The Reactions and Effects of Nitrogen in Steel, Trans. A. S. S. T., **8**, p. 291; 1925.

[5] Osawa, A., and Iwaizumi, S., X-ray Investigation of Iron and Nitrogen Alloys, Sci. Repts., Tohoku Imperial Univ., Sendai, Japan; Series I, 18, No. 1, 1929.

[6] Sawyer, C. B., Nitrogen in Steel, Trans. A. I. M. M. E., **49**, p. 799; 1923.

[7] All percentage figures for nitrogen used herein are by weight, not by volume.

[8] Andrew, J. H., The Influence of gases upon the Critical Ranges of the Iron Carbon Alloys, Iron & Steel Inst. Carnegie Schol. Mem., **3**, p. 236, 1911; Iron and Nitrogen, J. Iron & Steel Inst., **86**, p. 210; 1912.

determination of the iron-nitrogen diagram by the use of nitrided specimens may be likened to a hypothetical study of the iron-carbon diagram in which only carburized specimens were available, wherein not only one iron-carbide was formed but two or more, and in which much of the carbon escaped on heating and cooling.

Early in 1922, before either Sawyer's or Fry's work was published, the Bureau of Standards began a series of thermal analyses of nitrided specimens. While it soon became evident that thermal analysis alone is insufficient for establishing the relationships between iron and nitrogen, the work was continued as time permitted. Within the last year, however, the work has been more active and an attempt has been made, with the diagrams of Sawyer and Fry as a basis, supplemented by microscopic and X-ray examinations, together with the thermal analysis data, to resurvey some portions of the iron-nitrogen system.

No claim whatever is made that the present paper completely settles the iron-nitrogen constitution diagram. Some of the interpretations of the data are matters of opinion. In a system beset with so many difficulties, final conclusions can not be hastily drawn.
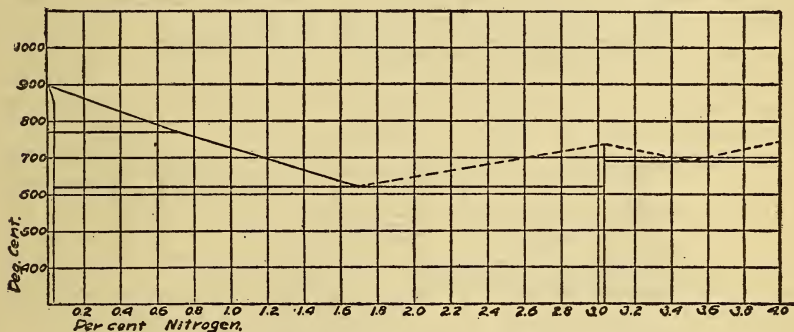

FIGURE 1.—*Sawyer's iron-nitrogen constitution diagram*

II. DISCUSSION OF SAWYER'S AND FRY'S DIAGRAMS

A brief discussion may here be given of the two existing diagrams of the iron-nitrogen system determined independently by Sawyer[9] and by Fry[10] at about the same time, in 1923. These diagrams are shown in Figures 1 and 2. Sawyer depended largely on thermal analysis, which he supplemented by microscopic examinations. Fry, on the other hand, in view of the previously mentioned difficulties involved in thermal analysis, avoided this method entirely and relied mainly on microscopic examinations. Fry worked with a 0.1 per cent carbon steel and Sawyer with very low carbon sheet iron.

On the lower nitrogen side of the diagram Sawyer and Fry are in substantial agreement. The diagram in this region closely resembles the iron-carbon diagram. Nitrogen, like carbon, lowers the A_3 point of iron and a eutectoid, Braunite,[11] a constituent named for one of the first to study this system, occurs similar to pearlite

[9] See footnote 6, p. 1006.
[10] See footnote 1, p. 1005.
[11] Braune, H., Influence De L'Azote Sur Le Fer et L'Acier, Rev. de Métallurgie, **2**, p. 498, 1905; **4**, p. 834; 1907. Stahl und Eisen, Ueber die Bedeutung des Stickstoff's im Eisen, **26**, p. 1357; 1906.

in steel, but contains about twice as much nitrogen as the carbon content in pearlite. Sawyer placed the nitrogen content of Braunite at 1.7 per cent, Fry at 1.5 per cent. The eutectoid horizontal in the iron-nitrogen system is about 100° C. lower than in the iron-carbon system. Sawyer placed it at 620° C. and Fry at 580° C. The solid solubility of nitrogen in iron at room temperature is quite
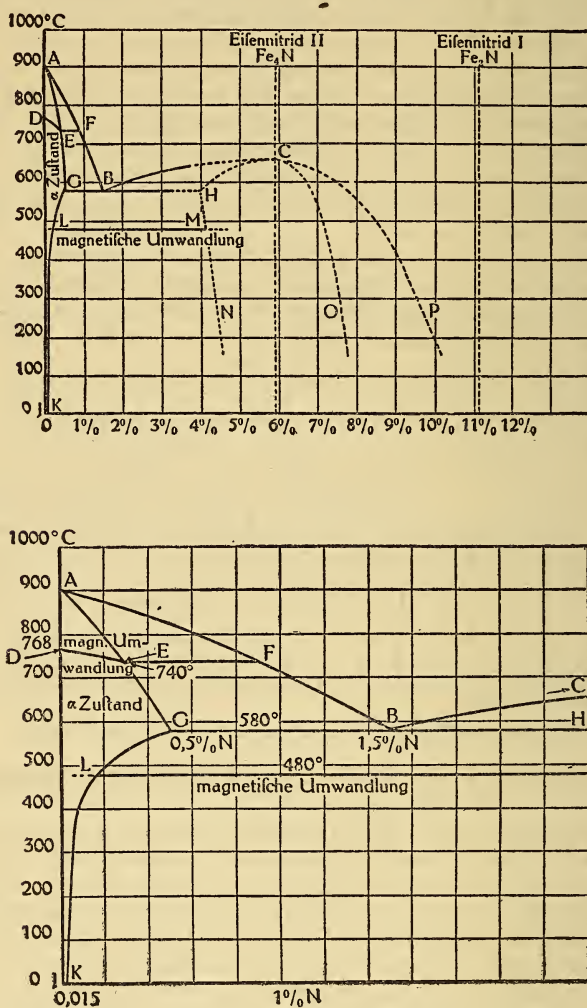

FIGURE 2.—*Fry's iron-nitrogen constitution diagram*

low, Sawyer placed it at 0.03 per cent and Fry at 0.015 per cent. This is somewhat higher than the solubility of carbon in iron at room temperature which is considered to be below 0.01 per cent.[12] Sawyer did not determine the solubility of nitrogen at the eutectoid horizontal, but Fry sets this at the very appreciable value of 0.5 per cent; in this respect there is considerable difference between the

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[12] Gillett, H. W., discussion of paper by M. A. Grossman on Oxygen Dissolved in Steel, and Its Influence on the Structure, presented at A. S. S. T. convention, 1928.

behavior of carbon and nitrogen, since the solubility of the former at the A_1 point is not very much higher than at room temperature, it being generally placed at about 0.035 per cent.

For alloys of higher nitrogen content Sawyer's and Fry's diagrams are at considerable variance, as may be briefly pointed out. Sawyer considered the nitrogen compound, which together with iron, forms the eutectoid, Braunite, to be Fe_8N whereas Fry considers it to be Fe_4N. Sawyer, from his thermal analyses and from microscopic evidence which will be discussed later, decided that there was another eutectoid transformation, which takes place at 690° C. between the compounds Fe_8N and Fe_6N. Fry's diagram does not contain this horizontal. Sawyer did not continue his diagram beyond the compound Fe_6N (4 per cent nitrogen), but Fry also included the compound Fe_2N (11.3 per cent nitrogen), which he indicated to be unstable.

Murakami concluded from his recent studies [13] that there are two iron-nitrogen compounds, Fe_2N and Fe_4N, corresponding to nitrides I and II described by Fry. His interpretation of the complete diagram is not yet available, however.

Fry also made magnetic measurements and placed a magnetic transformation horizontal across the lower nitrogen side of the diagram at 480° C. Indications of thermal transformations, in the form of "swings" instead of definite arrests, in this temperature range were obtained in the bureau's thermal analyses, but it is not certain that the magnetic transformation had any relationship to the low temperature "swings." The interpretation of these thermal effects was not sufficiently clear, however, to warrant representing them on the constitution diagram.

III. THERMAL ANALYSES

In order to obtain as uniform distribution of nitrogen as possible, Sawyer nitrided thin disks of sheet iron 0.228 mm thick which he piled on top of one another to form his thermal analysis specimens. At the bureau, after some preliminary work with solid pieces of iron, it was decided to use electrolytic iron crushed, before nitriding, into granules to pass through a 20-mesh sieve and in later work through a 30-mesh sieve.

The electrolytic iron cathodes used as raw material were first cleaned with hydrochloric acid if the surface was oxidized, washed with water and with alcohol, dried, and pulverized in a steel mortar to pass a 30-mesh sieve. In order to reduce any oxide present, the powdered iron was heated to 900° C. in oxygen-free and dry hydrogen for three hours or 950° C. for two hours and allowed to cool in the hydrogen. In nitriding, a 40 g sample of the reduced iron was placed in a thin layer in an alundum boat in an electric tube furnace, a thermocouple being inserted into the charge for temperature control.

A stream of very pure ammonia gas, further purified by passing through two towers, one containing soda lime and the other solid caustic potash, was passed through the furnace tube to displace the air. The furnace was then heated to the desired temperature, held there for the desired length of time, and the sample allowed to cool in the furnace, the flow of ammonia being maintained through the whole cycle. A flow gage at the exit end of the tube allowed maintenance of a constant flow of the gas.

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[13] See footnote 5, p. 1006.

In some of the experiments the samples, after nitriding, were heated in an atmosphere of nitrogen at definite temperatures and for a known period of time. Commercial nitrogen was passed over hot copper in a second tube furnace to remove oxygen, then through a phosphorus pentoxide tube for removal of water, and then through the soda lime and caustic potash towers and over the specimen in the tube furnace of the apparatus above described.

In order to obtain a compact specimen and to insure close contact with the thermocouple tip in the thermal analysis, the powdered nitrided iron was compressed in a steel die under 75,000 lbs./in.² pressure, into briquettes 0.26 by 0.32 by 0.50 inch. Specimens with an average nitrogen content of 2.4 per cent or less were strong enough so that they could be slotted with a hacksaw and handled as a solid specimen. With higher nitrogen, the briquettes would crumble in the fingers; hence the thermal runs on specimens showing 2.5 to 5 per cent nitrogen by analysis were made on the pulverulent samples packed tightly about the thermocouple bead in a small alundum crucible which was kept tightly covered.

Table 1 shows the conditions of nitriding and the nitrogen content of samples prepared, and also the time and temperature of heating for the specimens which were annealed in nitrogen.

TABLE 1.—*Nitriding conditions for specimens for thermal analyses*

Specimen No.	Nitriding conditions		Annealing		Nitrogen content [1]
	Temperature	Time at temperature in NH_3	Temperature	Period at temperature in nitrogen	
	°C.	*Hours*	°C.	*Hours*	*Per cent by weight*
21	400	½			0.02
23	400	1			.14
28	400	¾			.30
18	450	1			.20
8	450	3			[2].21
22	500	¼			.27
27	500	½			.81
29	500	½			.95
24	500	¾			2.12
25	550	¼	---------	(3)	.65
20	550	½			1.41
26	550	1			[4]2.47
7	550	2			3.00
5a	650	1			4.80
6	650	1			2.40
9	650	4			2.69
10	650	5			3.43
17	650	8			3.35
13		½	650	½	[5].50
14		¾	650	¾	1.30
15		¼	650	¼	[6]1.25
16		1	650	1	1.25
4	650	1	600	1	.19
3		1	750	1	.015
2		1	850	1	.02
1		1	950	1	.03
5		1	950	1	.01

[1] All nitrogen determinations, here and elsewhere, were made by L. Jordan, chemist, and associates.
[2] Sample 8, after thermal analysis (maximum temperature of thermal analysis run, 875° C.), contained 0.18 per cent nitrogen.
[3] Not annealed.
[4] Sample 26, after thermal analysis (maximum temperature of thermal analysis run, 1,030° C.), contained 0.04 per cent nitrogen.
[5] Sample 13, after thermal analysis (maximum temperature of thermal analysis run, over 930° C.), contained 0.20 per cent nitrogen.
[6] Sample 15, after thermal analysis (maximum temperature of thermal analysis run, 967° C.), contained 0.02 per cent nitrogen.

The amount of nitrogen taken up is obviously dependent on both time and temperature. It is probable also that the rate of flow through or the pressure in the furnace may influence the degree of nitriding. These factors were maintained as constant as possible, although the control was by no means perfect. With few exceptions (notably Nos. 5a and 14, and No. 4), the series is fairly self-consistent. In general, it appears that nitriding at 550° C. is nearly as rapid as at 650° C. It may be concluded from Table 1 that decomposition on heating in nitrogen at or below 650° C. was slow, but that at 750° C. or above it was rapid, being almost complete in an hour.

As shown in Table 1, sample No. 8, nitrided three hours at 450° C. (0.21 per cent nitrogen), retained almost all its nitrogen (0.18 per cent) after thermal analysis, and No. 13, containing 0.50 per cent nitrogen after being nitrided one-half hour at 650° C. and heated one-half hour in nitrogen at 650° C., retained 0.20 per cent after thermal analysis. This specimen, however, gave evidence of evolution of nitrogen while passing through its critical point at 600° C. as shown by the flow meter registering the passage of the stream of nitrogen out of thermal analysis tube.

On the other hand, No. 15, initially containing much more nitrogen than No. 13, showed almost none after thermal analysis, and No. 26 with about 2½ per cent nitrogen initially, lost almost all of this during thermal analysis. It seems, therefore, that an iron-nitrogen alloy produced by nitriding till only a low nitrogen content is attained is more stable on heating than the alloys corresponding to a relatively large percentage of nitrogen.

It is evident that, on account of decomposition during the heating run, the cooling curves will not all represent the initial nitrogen content and that most of the cooling curves may represent iron which is practically nitrogen-free. The decomposition might also be expected to change the compactness and size of the briquette so that less intimate thermal contact might result between thermocouple bead and briquette in the upper part of the heating curve as well as on the cooling curve.

The inverse rate thermal analysis apparatus and methods used at the Bureau of Standards have been described by Scott and Freeman [14] and by French.[15]

The thermal curves obtained with the unannealed specimens listed in Table 1 are shown in Figure 3. No effect due to nitrogen was visible with 0.02 per cent nitrogen. With 0.14 per cent nitrogen a definite point appeared at about 600° to 620° C. With 0.21 per cent nitrogen the low temperature swing appeared on a run not reproduced in Figure 3, the 600° to 620° C. point also appearing. With 0.27 per cent only the 605° C. point appeared. With 0.30 per cent nitrogen a sharp low temperature swing occurred, but the lower part of the curve is of doubtful reliability, as it does not show the proper shape. The point appearing at 590° to 620° C. was shown by all subsequent curves, through 0.95 per cent nitrogen.

With 1.41 per cent nitrogen the 590° to 620° C. point appeared and a higher temperature point also. With 2.40 per cent nitrogen the

[14] Scott, H., and Freeman, J. R., jr., Use of a Modified Rosenhain Furnace for Thermal Analysis, B. S. Sci. Paper No. 348, 1919.
[15] French, H. J., A Recording Chronograph for the Inverse-Rate Method of Thermal Analysis, B. S. Tech. Paper No. 230, 1923.
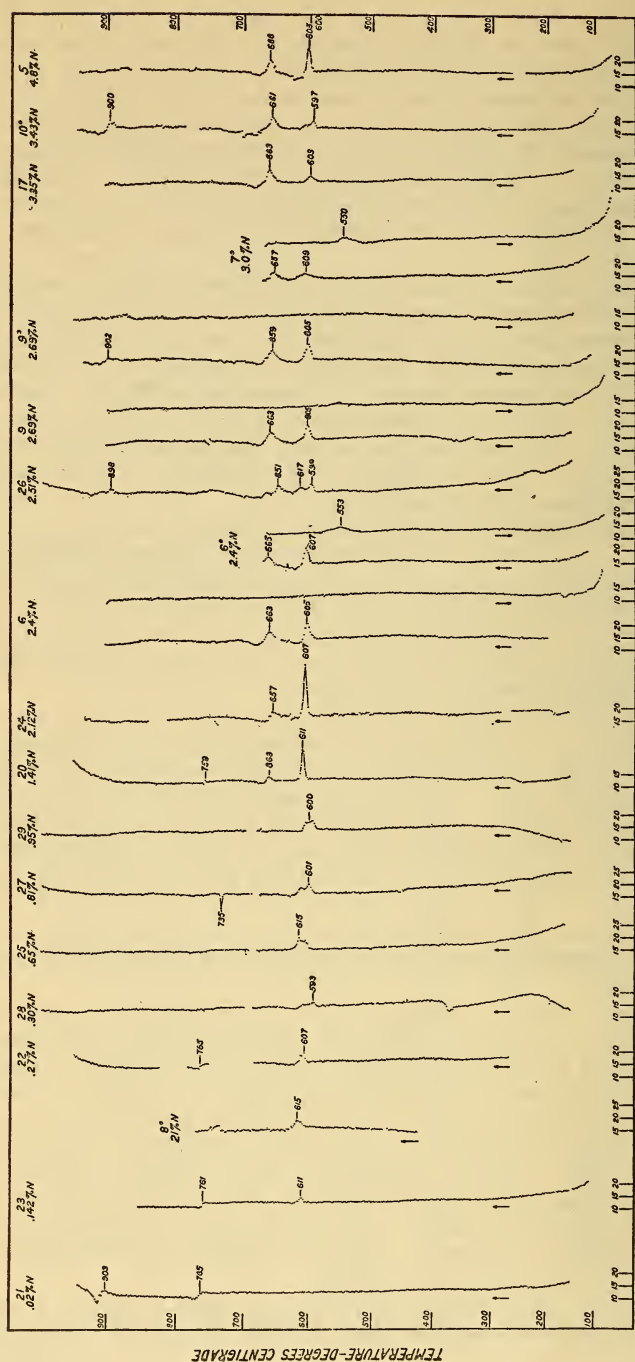
FIGURE 3.—*Thermal analysis curves of nitrided electrolytic iron granules*

These specimens were not annealed in nitrogen after the nitriding treatment.

cooling curve (specimen No. 6, fig. 3), like those of all the lower nitrogen specimens of this series taken after the temperature has been raised to 900° C. or above, showed no effect of nitrogen. A duplicate (first) run on a second sample of No. 6° carried only to 670° C. showed a point on cooling (fig. 3), thus indicating that there is a certain reversibility of the thermal effect due to nitrogen if the nitrogen is not lost by decomposition. Throughout the rest of the series the 590° to 620° C. point and the higher temperature point that first appeared with 2.40 per cent nitrogen were observed.

The thermal curves obtained with specimens annealed in nitrogen after nitriding (Table 1) are shown in Figure 4. The results obtained with samples containing 0.03 per cent nitrogen or less are not consistent. In this range of nitrogen content, if the specimens were uniform throughout each grain, according to Sawyer, the nitrogen would be in solid solution at all temperatures, and, according to Fry, would be in solid solution above 400° C.

With samples of a higher nitrogen content, No. 4 (0.19 per cent nitrogen), Figure 4, doubtful swings and sharply marked double points were noted. This was heated only to 675° C. and the cooling curve again showed a doubtful swing. No. 13 with 0.50 per cent nitrogen was one of the most interesting specimens. A point of marked intensity, comparable to A_1, was observed which strongly indicated the presence of a definite eutectoid. On duplicate runs the heating curves of Nos. 13 and 13° (fig. 4) gave identical results, but the cooling curves showed no sign whatever of any effect of nitrogen. During the heating of Nos. 13 and 13°, copious evolution of nitrogen took place as the sample passed through the point at 600° C.

The average nitrogen content of this specimen, 0.50 per cent, happens to coincide with the limit of solubility of nitrogen in ferrite at 0.50 per cent shown by Fry. The temperature, however, was 605° C. against Fry's figure of 580° C., established by quenching and metallographic examination of the quenched specimens rather than by heating curves. Since the 0.50 per cent refers to average nitrogen content, it is not likely that the specimen really represents that composition on Fry's diagram.

The critical ranges on heating found in the unannealed nitrided series of Figures 3 and of the nitrided and annealed series of Figure 4 are shown in Figure 5, in which circles show the maxima of the runs on samples not annealed and crosses those of the annealed series. The length of the vertical lines shows the width of the temperature range. The points group themselves, for specimens with 1.25 per cent nitrogen and above, quite definitely about two temperatures, 660° and 605° C., and the ranges always pass through those temperatures.

It will be observed that the A_3 point in alloys of high initial nitrogen content is very much weaker in both heating and cooling curves than is normal for electrolytic iron, and that while the method appears sensitive enough to show A_2 even on briquetted specimens, in many cases neither A_2 nor A_3 was detected.

Nitriding in the nitrogen-hydrogen mixture resulting from the cracking of ammonia might be expected to result in the removal by hydrogen of the carbon and oxygen present in electrolytic iron. The upper end of the heating curve and the cooling curve should, therefore, represent iron more or less purified from carbon and
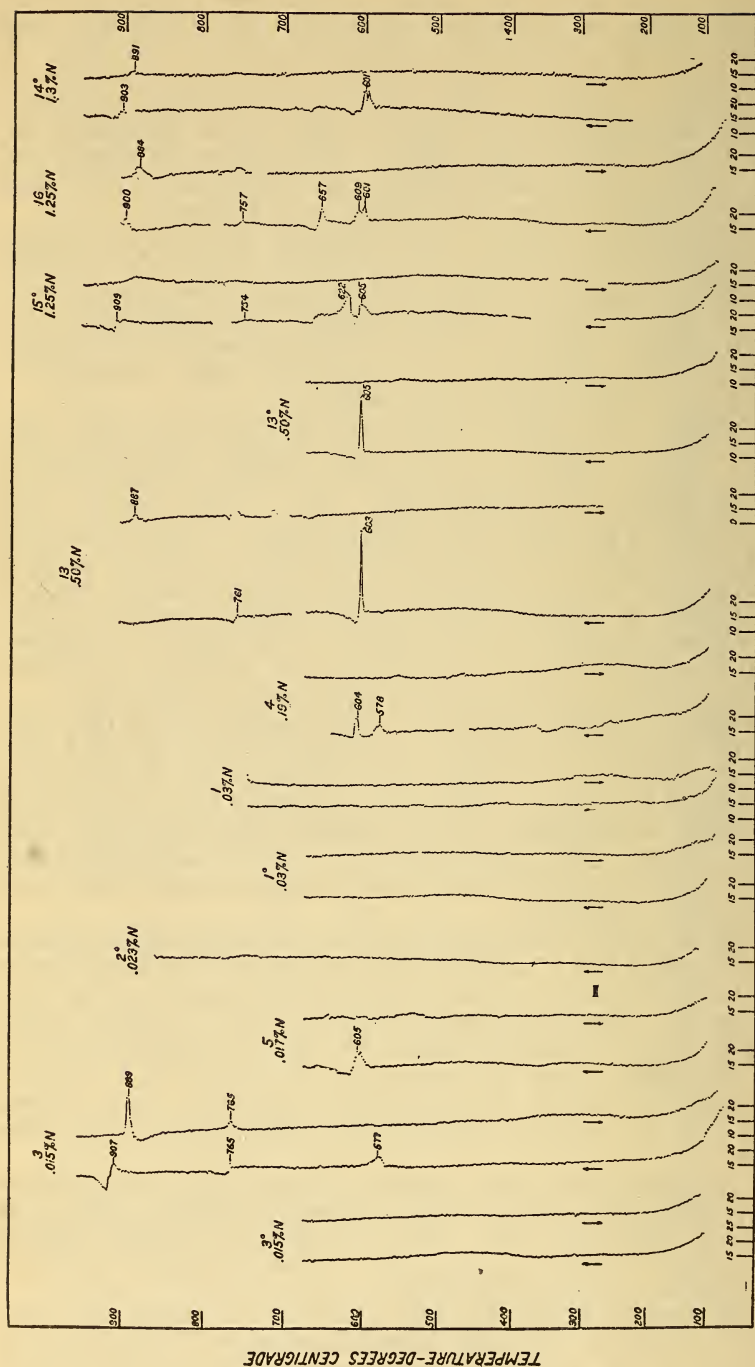
FIGURE 4.—Thermal analysis curves of nitrided electrolytic iron granules

These specimens were annealed in nitrogen after the nitriding treatment.

oxygen, but contaminated with some nitrogen. Since Yensen [16] argues that pure iron free from carbon and oxygen should have no transformations, these thermal analyses indicate that Yensen's hypothesis deserves respectful consideration.

As shown in Figure 5, Sawyer's two arrests in higher nitrogen alloys were confirmed. The lower one, which undoubtedly represents the Braunite eutectoid transformation, may be set from these results at 605° C. The upper horizontal which occurred only in alloys of average composition, 1.25 per cent nitrogen or higher, may be set at 660° C. As will be discussed later, microscopic examination indicated that this upper transformation could not be due to another eutectoid on the higher side of the diagram as Sawyer decided, but that it was probably due to a peritectoid reaction above the eutectoid horizontal.

Another point on which the thermal analyses throw some light is the solid solubility of nitrogen in iron. In iron containing 0.2 per cent average nitrogen (specimen 4, fig. 4) the arrest in the eutectoid transformation range was not sharp, as in iron containing 0.5 per cent average nitrogen (specimen 13, fig. 4), but was doubled. A possible interpretation of this is that the lower portion of the double transformation represents the solution of the nitride in alpha iron and the upper portion the eutectoid transformation of that zone of the specimen having a higher nitrogen content. If this view is correct, it would indicate appreciable solubility of nitrogen in iron at the eutectoid transformation temperature, and thus partly substantiate Fry's figure of 0.5 per cent. That a definite arrest was obtained in the specimen of 0.5 per cent average nitrogen content can not be considered as evidence that no more than this content is soluble, because of the lack of uniformity in the composition of the specimens. In this range the average nitrogen content appears to be roughly only about a third of that of the outer layer.

IV. MICROSCOPIC EXAMINATION

In examining under the microscope sections of the granules used in the thermal analyses the two layers described by Fry as Nitride I and Nitride II and considered by him to be solid solutions of the compounds Fe_2N and Fe_4N, respectively, were recognized. However, no eutectoid between the two layers was found such as Sawyer reported. His explanation that the upper horizontal shown by thermal analysis represented a eutectoid transformation can only hold if such a eutectoid exists. The other possible way of accounting for the upper horizontal—namely, that it represents a peritectoid reaction— is therefore suggested. Such an explanation, however, calls for the presence of another compound, as shown in Figure 20. In examining blocks of remelted electrolytic iron specially nitrided for the purposes of microscopic examination, an extreme outer layer not hitherto observed in the granules and not described by Fry was detected. At first this surface layer was thought to be due to oxide resulting from moisture in the ammonia gas used, but as it still appeared after the ammonia had been dried with metallic sodium, it was decided to be another nitride layer. The support this gave to the supposition that the upper horizontal represented a peritectoid reaction was

[16] Yensen, T. D., Pure Iron and Allotropic Transformations. Tech. Pub., 185, Amer. Inst. Min. & Met. Engrn.; February, 1929.

INITIAL AVERAGE COMPOSITION OF WHOLE SAMPLE
PER CENT NITROGEN

685° END
660° MAXIMUM
640° BEGIN
625° END
605° MAXIMUM
590° BEGIN

o—NITRIDED BUT NOT ANNEALED
x—NITRIDED AND ANNEALED
VERTICAL LINES INDICATE TEMPERATURE
RANGES OF TRANSFORMATIONS
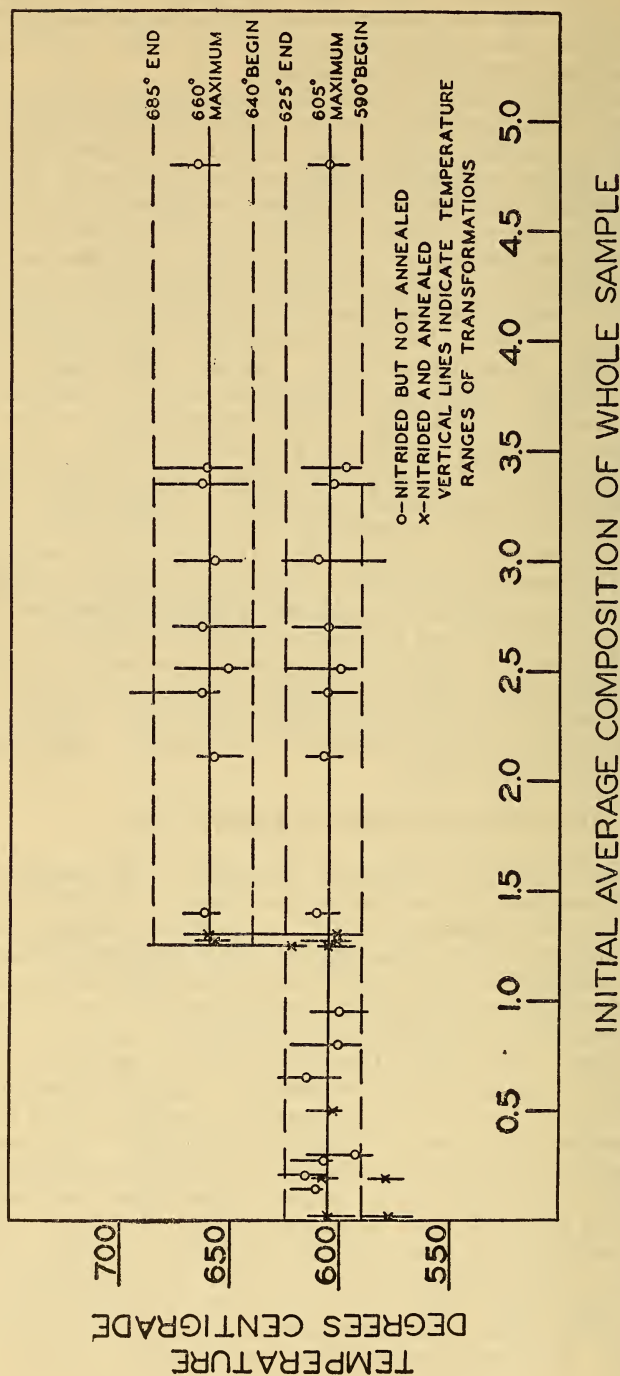
TEMPERATURE
DEGREES CENTIGRADE

FIGURE 5.—*Summary of thermal analysis curves*

The points indicate arrests on the inverse rate heating curves.

recognized, and the regions in the diagram on both sides of this line were explored by microscopic examination for further confirmation.

The details of the microscopic examination will now be described. Figure 6 shows the appearance of sections through the granules of two thermal analysis specimens. The structures shown are representative, in regard to uniformity and depth of nitriding, of all the thermal analysis specimens. The nitrogen penetration was not uniform, most of it being concentrated in the surface layers.

Figure 7 shows the structure of a specimen which chemical analysis showed to contain only 0.01 per cent average nitrogen. The presence of what appear to be nitride needles is of interest, for it may indicate that the solid solubility of nitrogen in iron may be lower than the value, 0.015 per cent, given by Fry. It should be remembered, however, that too great reliance can not be placed in the values obtained for nitrogen content due to lack of homogeneity of the specimens.

The layers designated in Fry's micrographs as Nitride I and Nitride II may be seen in Figure 8, the thicker outer layer being Nitride I. The outer layer is light brown in color and is not appreciably attacked by 5 per cent alcoholic picric acid. The thin inner layer is a lighter cream color, is attacked by picric acid, and also is colored dark brown by boiling sodium picrate; it exhibits twinning as was noted by Fry and Sawyer. A characteristic of this inner layer, which apparently has not been previously noted, is its marked tendency to form slip lines, as shown. These probably arose when the granules were compressed into the briquettes used for thermal analysis. It appeared evident from the etching characteristics of the nitride needles that, as has also been noted by Fry, they are composed of the same constituent as the inner layer.

In the specimens nitrided below 600° C. only the two layers and the nitride needles were present. In those nitrided above 600° C., however, the eutectoid, Braunite, also appeared. This is the dark constituent, resembling pearlite, shown in Figure 9. It always appeared on the interior side of Nitride II; without doubt, Braunite is a eutectoid of this compound and iron. Figure 9 (*b*) depicts a nitrided specimen annealed in vacuum at 685° C., after which it contained 0.5 per cent average nitrogen. The specimen was composed of approximately one-third eutectoid, and this, therefore, roughly confirms Sawyer's and Fry's values for the eutectoid composition of 1.5 per cent nitrogen.

Thus far only the structures of the electrolytic iron granules used for thermal analysis have been considered. Since it was difficult to prepare these granules satisfactorily for microscopic examination, small blocks of remelted electrolytic iron were nitrided and used. These were mounted in solder before polishing so that the sections could be observed to the extreme edge. The specimens were not ground on an abrasive wheel but were smoothed on emery paper laid on a board, this precaution being taken in order not to break off the nitrided layers.

In these nitrided blocks an outer layer not described by Fry, lying outside the layer designated in his micrographs as Nitride I, was detected. The appearance of this layer, which has a eutectoid structure, is shown in Figures 10 and 11; in these and subsequent figures the outer nitride layer is at the top or at the left of the micro-

graphs. In examining nitrided electrolytic iron specimens received from another laboratory, the outside layer was observed and found to contain an oxide constituent as shown in Figure 12. It is evident, however, that the whole outer layer can not be attributed to oxide since, as previously mentioned, specimens nitrided in ammonia completely freed from moisture showed the outer layer. The color of the lamellæ and globules present in the outer layer, in the unetched state somewhat resembles that of iron oxide although the layer is considerably lighter and can readily be distinguished from iron oxide by etching.

This extreme outer layer was not noted by Fry, perhaps, on account of the rounding and cracking of the edges of his polished sections, but more probably because at the high temperature (680° C.) at which the specimens shown in his micrographs were nitrided the outer constituent is decomposed and only voids and fissures remain in its place. This is indicated by some of Fry's micrographs. The "decomposed appearance" of the structure of the outer layer upon nitriding at 600° C. or higher is shown in Figure 13.

Since this newly found layer has a eutectoid structure, the question may arise whether it is not the eutectoid which Sawyer considered to be formed at the upper horizontal. The evidence indicated very strongly, however, that this is not so. The layer is at the extreme outside and can not, therefore, be a eutectoid between the two inner nitride compounds as indicated in Sawyer's diagram. Moreover, the eutectoid structure of this outermost layer is already well marked at temperatures as low as 425° C. (see fig. 10 (*b*)), much below the temperature of the upper horizontal (660° C.). In fact, upon heating to a temperature as high as this the eutectoid structure of the outer layer disappears, due to decomposition.

A number of specimens were heated above the temperature of the upper horizontal and slowly cooled, but, as shown in Figures 14 and 15, no eutectoid could be detected between the two inner nitride layers, as is required by Sawyer's diagram. That these specimens had actually passed through a transformation, upon heating to the temperatures used in these tests, was evident from the disappearance of the inner layer (fig. 16 (*c*)) upon quenching the specimens above the transformation temperature. According to Sawyer's diagram, on the assumption of a eutectoid transformation, this inner layer should not disappear on heating to a temperature above the transformation, except at the exact eutectoid composition itself. On the assumption of a peritectoid transformation, however, as shown in Figure 20 the inner layer should disappear entirely on heating through the transformation. This evidence, therefore, together with the fact that three layers were found as called for in the construction of a diagram such as Figure 20, involving a peritectoid transformation, indicated strongly that the upper temperature horizontal represented a peritectoid transformation.

Figure 17 shows the results of tests made to determine the upper solubility or "stability" limit of the most stable nitride layer, namely, the yellowish layer not attacked by picric acid or sodium picrate, designated by Fry as Nitride I. Upon heating in an atmosphere of ammonia to 785° C., this layer still remained undecomposed, but at 815° C. the structure after quenching showed that decomposition was practically complete. The solubility or decomposition limit may,
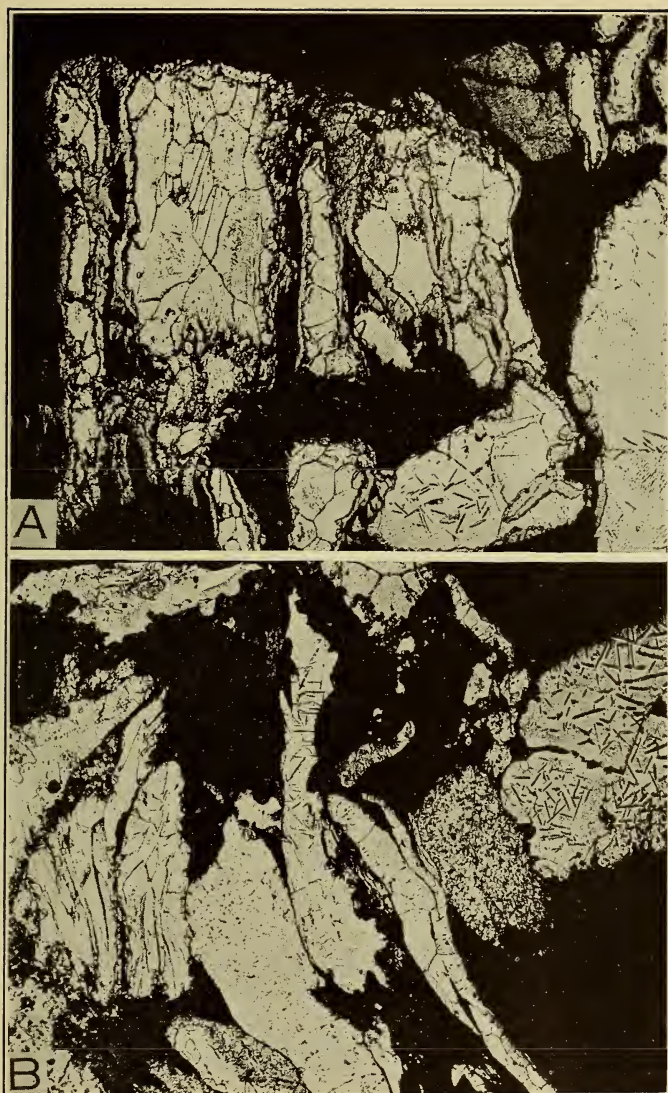
FIGURE 6.—*Nonuniform penetration of nitrogen in nitrided electrolytic iron granules used for thermal analyses,* × 100

The etching reagent in all of the micrographs was 5 per cent picric acid in alcohol, unless otherwise stated. *a,* Specimen No. 7 nitrided at 550° C. for two hours; average nitrogen content 3 per cent.   It was evident that the bulk of the nitrogen in this specimen was concentrated in the thin surface layers; *b,* specimen No. **13** nitrided at 650° C. for one-half hour; average nitrogen content 0.5 per cent.

FIGURE 7.—*What appear to be nitride needles in a specimen very low in nitrogen,* $\times$ *500*

Specimen 5a nitrided at 950° C. for one hour, then annealed at 950° C. in nitrogen for one hour; average nitrogen content 0.01 per cent.
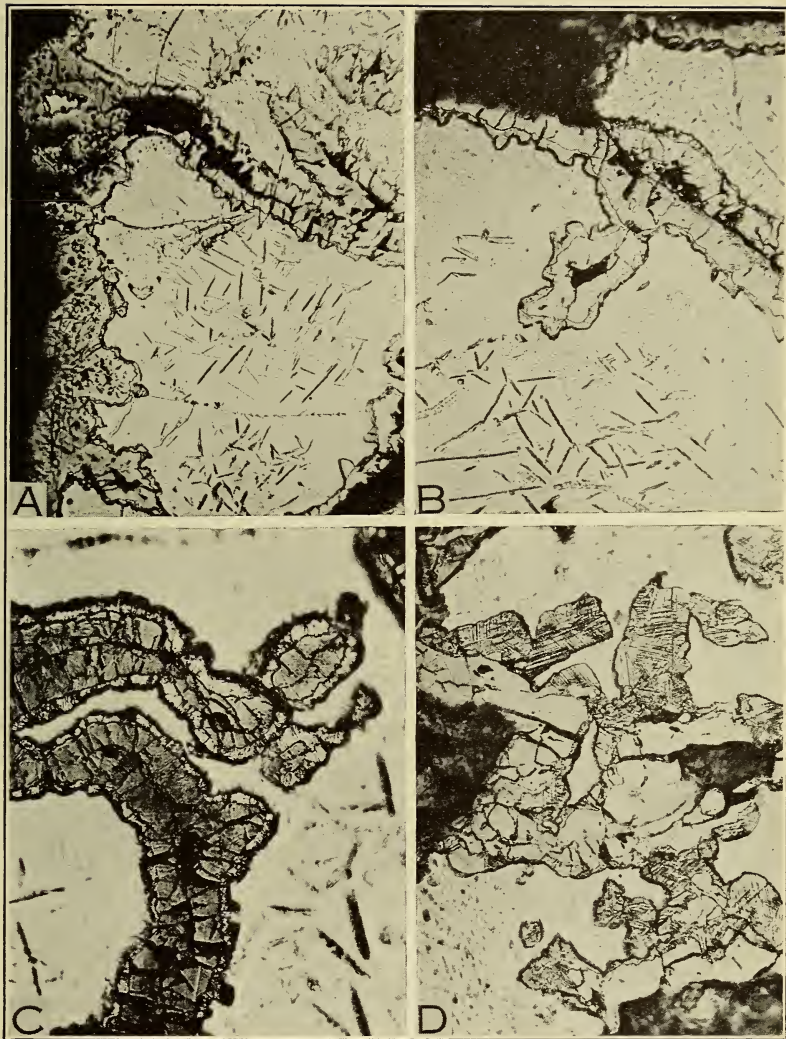
FIGURE 8.—*Layers in nitrided electrolytic iron granules*

a, Specimen No. 7 nitrided at 550° C. for two hours; there is a fairly thick outer layer, and a thin ribbon of an inner layer can be distinguished, × 250; b, same as a, × 500; c, the same specimen more deeply etched. This micrograph was taken not at the surface of the granule, but at a crevice along which the nitrogen penetrated. The "inner layer" is, of course, the one adjacent to the electrolytic iron (the pure white constituent containing the nitride needles and somewhat out of focus) while the "outer layer" extends on both sides of the crevice. Even after the rather prolonged etching the outer layer remained unattacked. In the inner layer what appears to be a twinned structure can be distinguished, × 500; d, specimen No. 10 nitrided at 550° C. for five hours. The outer layer may be recognized by its smooth appearance; it is not attacked by the etching solution. The inner layer is covered with a series of slip lines.
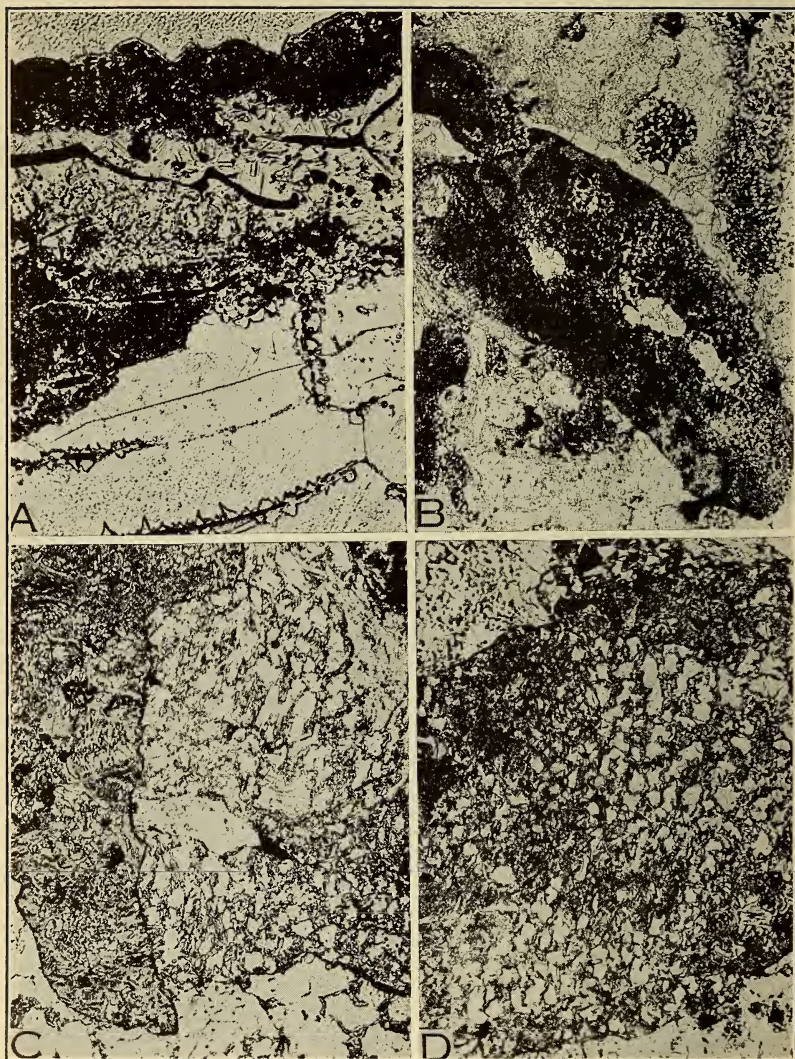
FIGURE 9.—*The eutectoid braunite containing about 1.5 per cent nitrogen*

a, Specimen No. 6 nitrided at 650° C. for one hour; average nitrogen content 2.4 per cent, × 500. The background at the top and bottom of the micrograph is the core of electrolytic iron. The dark constituent is the eutectoid braunite. The white constituent, appearing as a layer showing twins and as the sharply defined globular particles strung along the cracks and grain boundaries at the bottom of the micrograph is the "inner layer"; *b*, specimen No. 10 nitrided at 550° C. for five hours and then annealed at 685° C. in vacuum; average nitrogen content 0.49 per cent, × 100; *c*, same as *b*, × 500; *d*, specimen No. 9 nitrided at 650° C., then annealed at 685° C. in vacuum. The dark constituent is braunite.
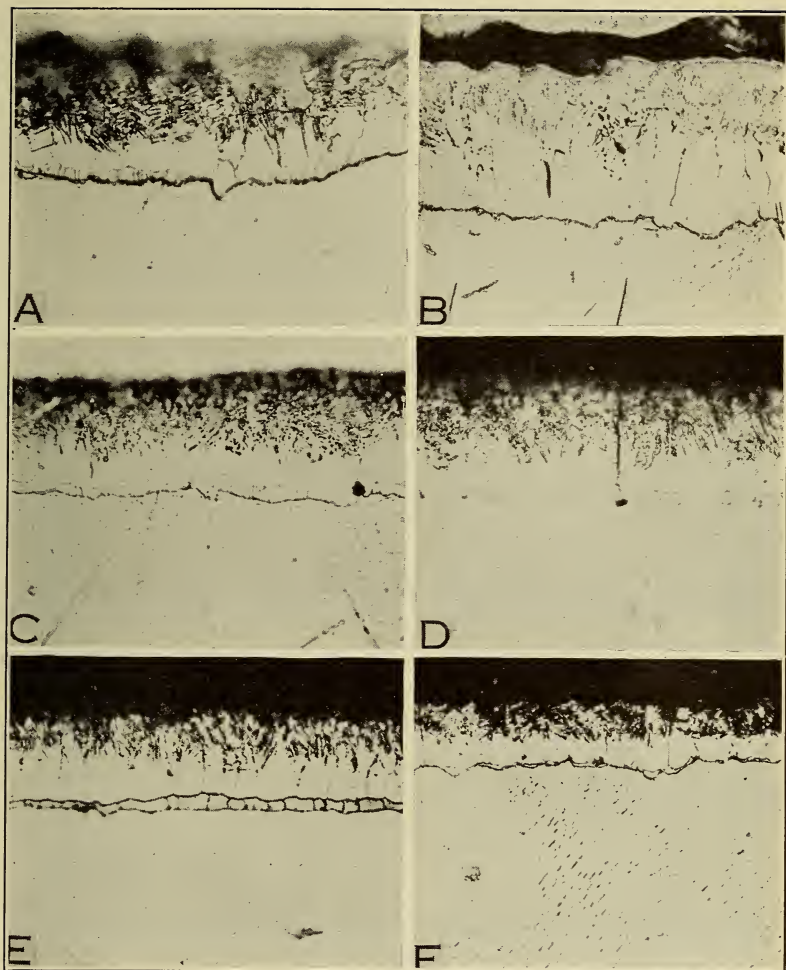
FIGURE 10.—*Appearance of nitrided layers in remelted electrolytic iron blocks,* × *500*

Three distinct nitride layers can be distinguished. The extreme outer layer has previously not been noted. As may be seen below, the nitriding temperatures of the specimens which showed a well-defined extreme outer layer were rather low, 550° C. or lower. *a*, Nitrided 75 hours at 500° C.; *b*, nitrided 25 hours at 550° C.; *c*, nitrided 25 hours at 550° C.; *d*, nitrided 75 hours at 500° C., etched in alkaline sodium picrate; *e*, nitrided 25 hours at 550°C.; etched in alkaline sodium picrate; *f*, nitrided 170 hours at 425° C. Boiling alkaline sodium picrate etches the inner layer brown or dark brown depending on the length of etching. The extreme outer layer has the appearance of a eutectoid and is etched by both picric acid and sodium picrate.
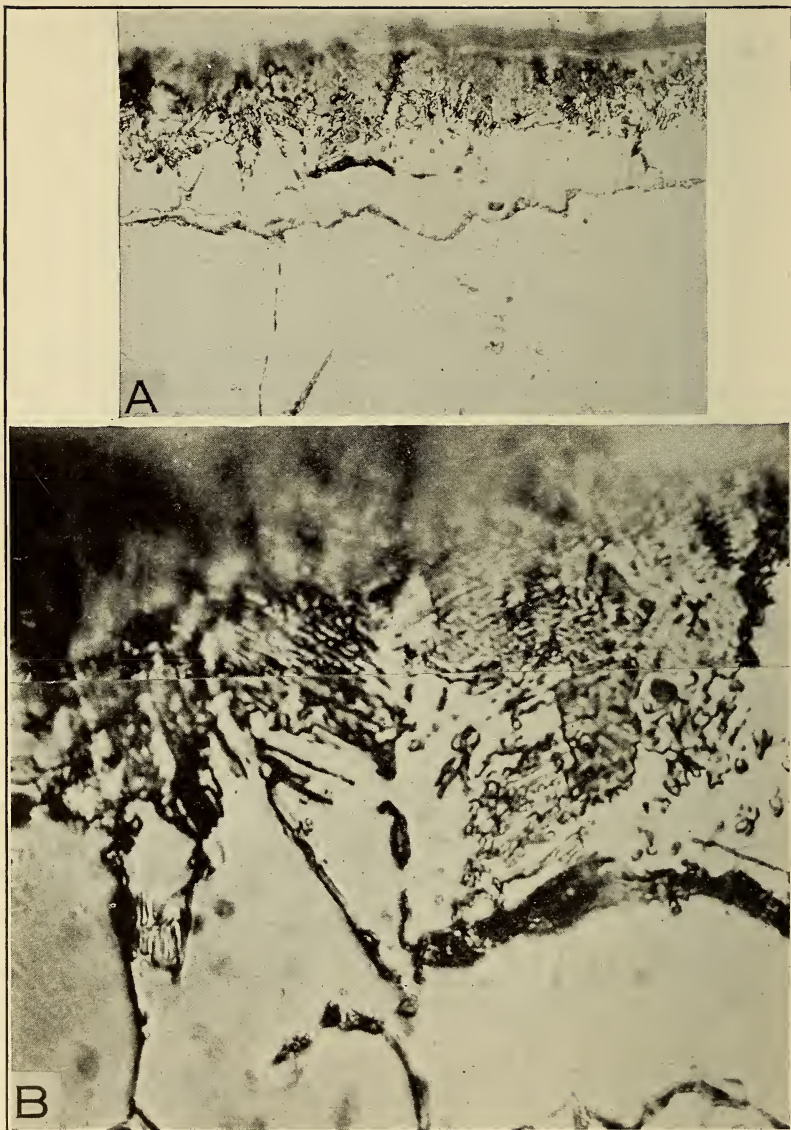
FIGURE 11.—*Appearance of extreme outer layer of nitrided iron block*
a, Nitrided 75 hours at 500° C., × 500; *b*, same spot, × 2,000.

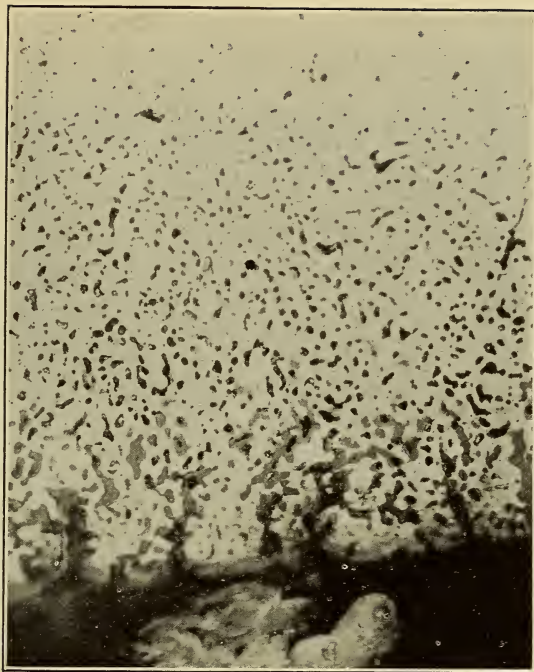FIGURE 12.—*Oxide constituent at surface of nitrided iron block,* × *500*

The edge of the specimen is at the left side. The dark gray constituent lining the cracks and voids was evidently iron oxide.
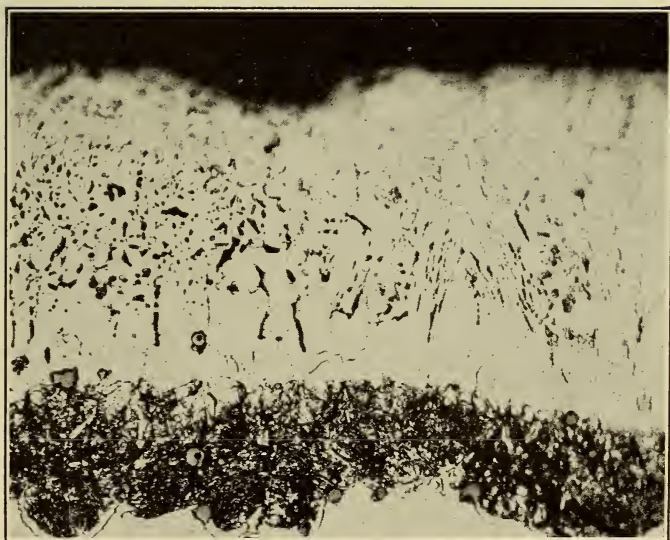

FIGURE 13.—*Apparent decomposition of extreme outer nitride layer,* × *500*

Nitrided 25 hours at 600° C. The voids and fissures in the extreme outer layer indicate the decomposition of the outermost constituent.

FIGURE 14.—*Appearance of nitrided iron blocks heated above upper horizontal and slowly cooled,* × 500

a, Nitrided 25 hours at 600° C., then heated one-half hour in NH₃ at 685° C. and furnace cooled; *b,* same as *a,* etched with sodium picrate; *c,* nitrided 75 hours at 500° C., then heated one-half hour in NH₃ at 685° C. and furnace cooled; *d,* same as *c,* etched with sodium picrate. At the bottom of each micrograph the eutectoid braunite is shown; this etches darker with picric acid than with sodium picrate; the inner nitride layer is etched a dark brown by the latter reagent. No signs of the formation of a eutectoid between the two inner nitride layers can be detected.
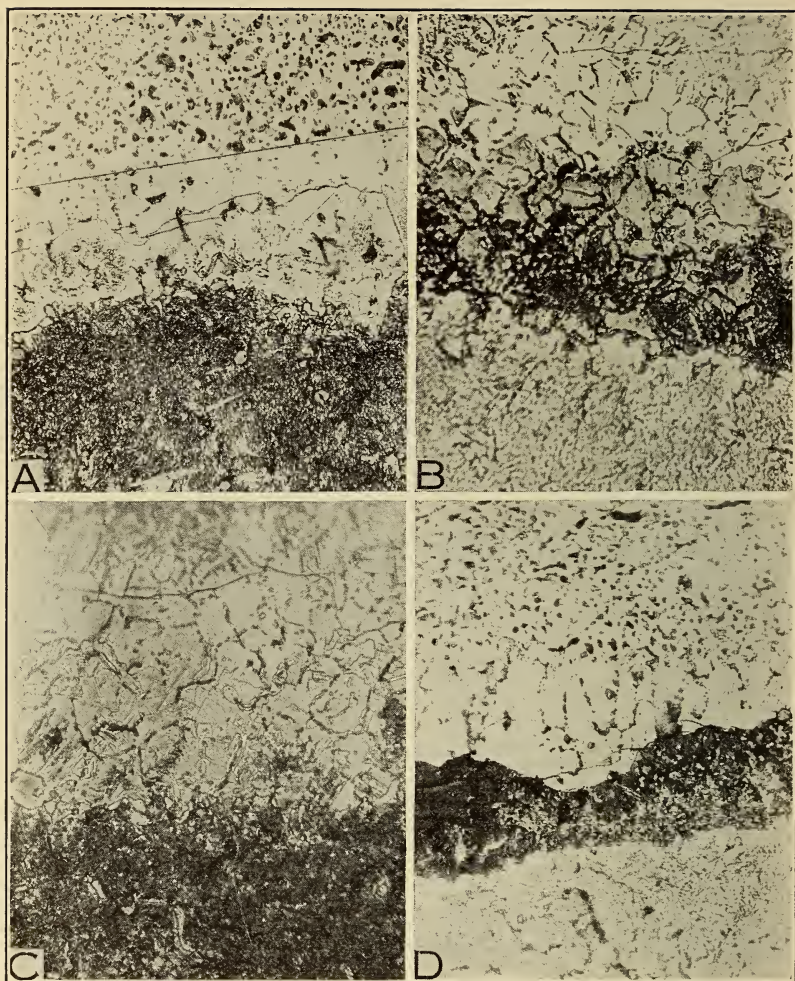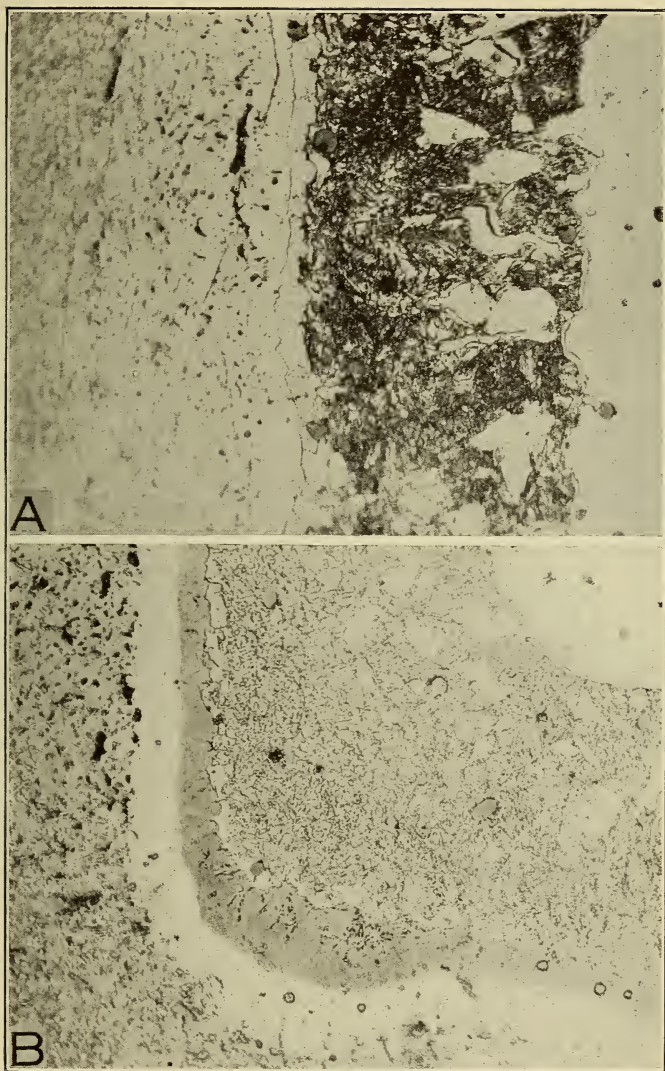
FIGURE 15.—*Appearance of nitrided iron blocks heated above upper horizontal and slowly cooled,* × 500

a, Nitrided 50 hours at 500° C., then heated one-half hour in NH₃ at 725°C., and furnace cooled. The edge of the specimen is at the left; *b,* nitrided 25 hours at 600° C., then heated one-half hour in NH₃ at 725° C. and furnace cooled; etched with sodium picrate. It is quite plain that no eutectoid was formed between the two inner nitrided layers.
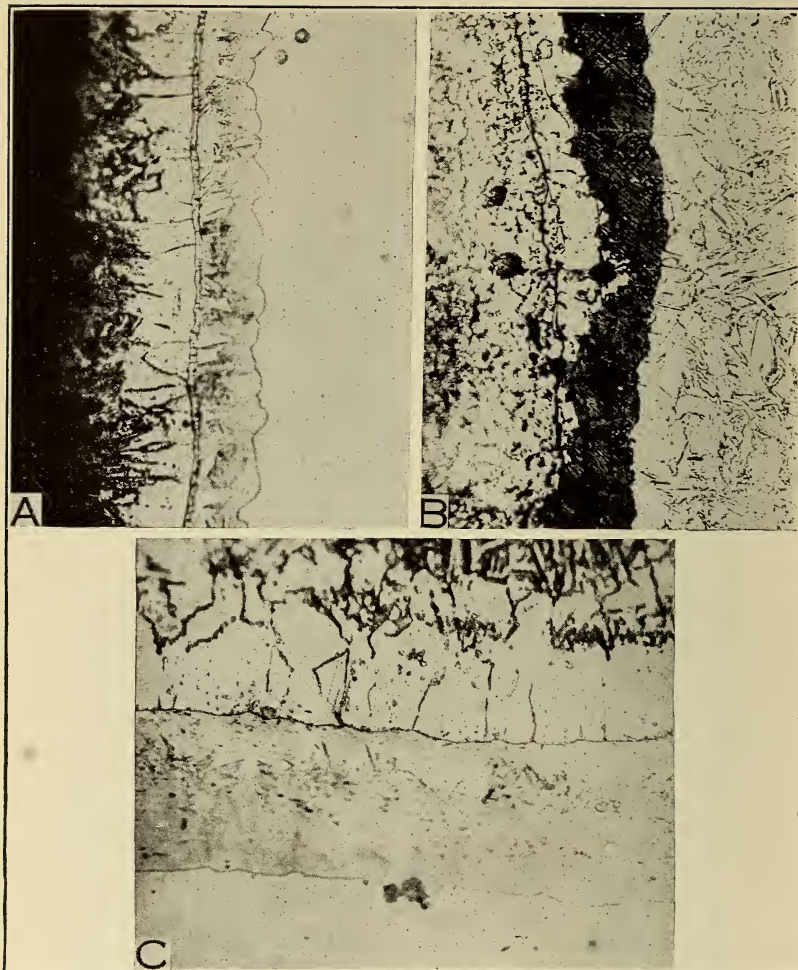
FIGURE 16.—*Appearance of specimens quenched from below and above upper horizontal,* $\times$ *500*

Etched with sodium picrate. *a*, Nitrided 75 hours at 500° C., then heated for one-half hour in NH₃ at 625° C., and quenched in water. The thin layer is the inner compound; the layer to the right corresponds to the eutectoid layer, but is martensitic due to quenching. A similar layer is shown in the other two micrographs of this figure; *b*, nitrided 75 hours at 500° C., heated to 685° C. in NH₃, slowly cooled to 625° C., held at this temperature for one-half hour and water quenched. The inner layer darkly etched and showing slip lines is again present, having become a good deal wider as a result of the heating to 685° C; *c*, nitrided at 500° C. for 75 hours, heated to 685° C. for one-half hour in NH₃, and quenched in water. The inner layer which etches dark with sodium picrate is no longer present.
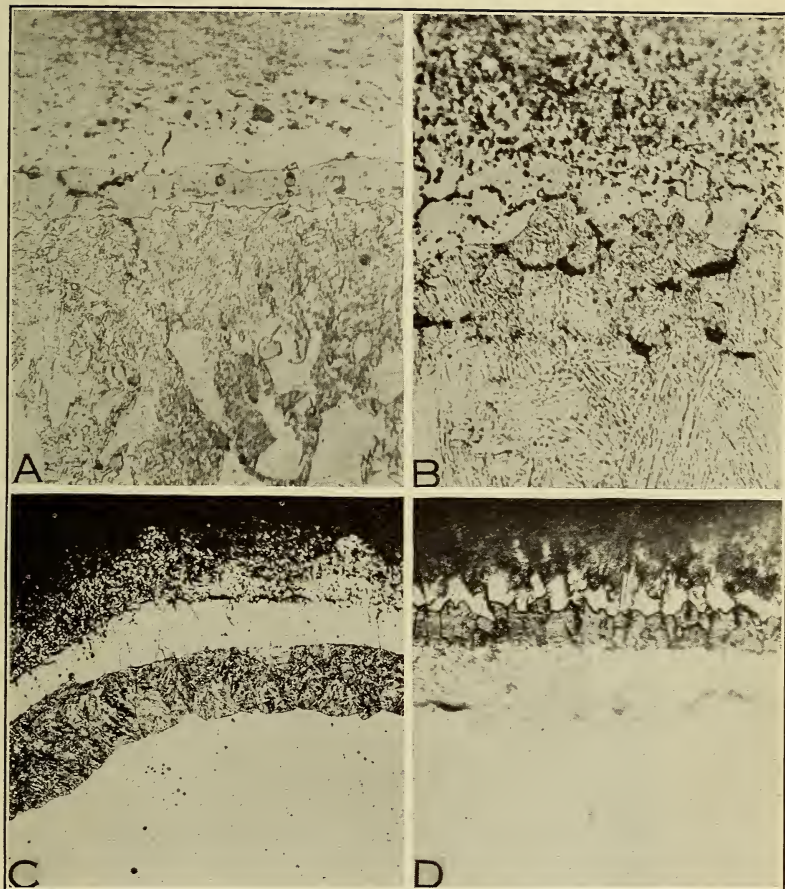
FIGURE 17.—*Determination of upper solubility limit of the more stable nitride layer*

a, Nitrided 75 hours at 500° C., then heated in NH₃ at 785° C. for one-half hour and slowly cooled in furnace; etched with sodium picrate. The lighter colored nitride layer is still intact, × 500; *b,* same as *a,* but quenched in water from 785° C. The light colored layer is still intact, × 500; *c,* nitrided 75 hours at 500° C., heated one-half hour in NH₃ at 815° C. and quenched in water. The middle layer of the three shown is ferrite, indicating decomposition of the nitride layers, × 100; *d,* nitrided 75 hours at 500° C., heated one-half hour in charcoal at 625° C.; the nitride layers appear to be stable, × 500.
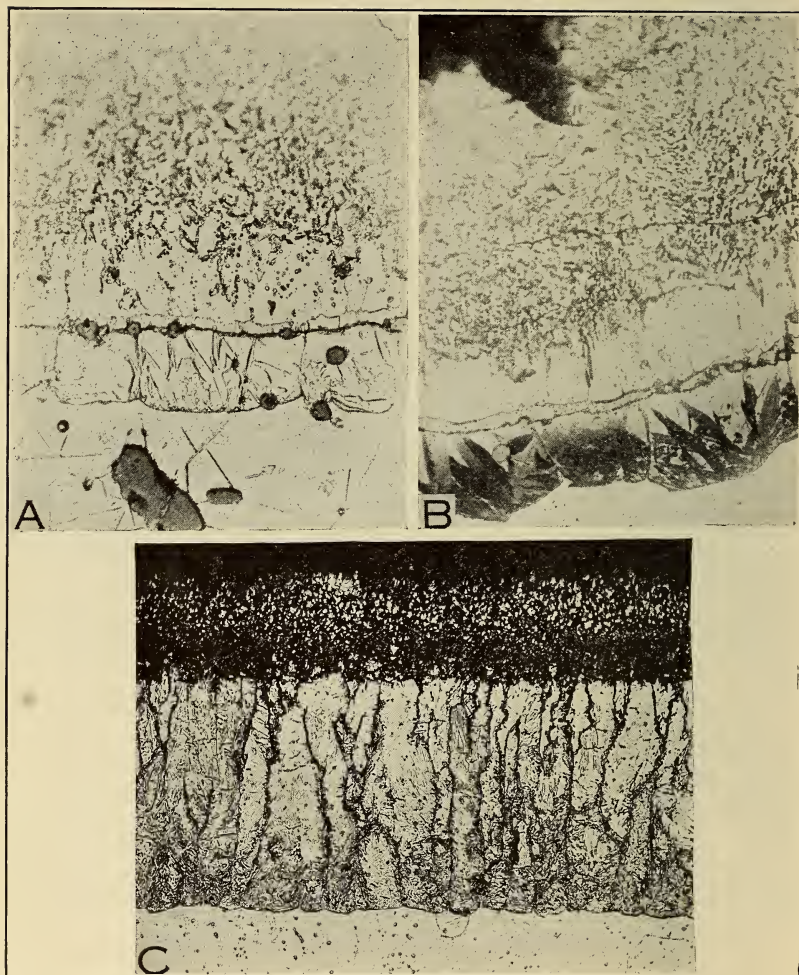
FIGURE 18.—*Martensitic structures obtained on cooling in air from above braunite eutectoid line*

a, Nitrided 25 hours at 600° C., air cooled, × 500; b, same as a, etched with sodium picrate; c, nitrided 25 hours at 700° C., and air cooled, × 100.

Figure 19.—*Same as Figure 18 c*, × *500*

therefore, be placed at about 800° C.   Nitride layers are undoubtedly
more stable in an atmosphere of ammonia than in the absence of
ammonia.   Figure 17 (*d*) shows the structure of a nitrided specimen,
packed in charcoal, heated to 625° C., and slowly cooled.   The two
inner nitride layers were stable at this temperature even in the
absence of ammonia.

Figures 18 and 19 show the martensitic condition which forms in
the Braunite layer upon fairly rapid cooling in air.   The marten-
sitic needles due to nitrogen appear to be very similar to those in
carbon steel.   The structures shown in Figure 19 also indicate that
just as the forms of martensite differ in high and low carbon steels,
so in this "nitrogen martensite" the structure toward the higher
nitrogen side of the layer is noticeably different from that toward the
lower nitrogen side.   In high carbon steels austenite is usually re-
tained with the martensite and analogously in the nitrogen alloy the
structure of the higher nitrogen side of the layer shown in Figure 19
also indicates the presence of an austenitic constituent.

V. X-RAY DIFFRACTION ANALYSES

X-ray analyses of the crystal structure of several of the specimens
of nitrided electrolytic iron granules and of the nitrided electrolytic
iron blocks were made by using a General Electric Co. X-ray diffrac-
tion apparatus and molybdenum *K* alpha radiation.   Particles of
the nitrided granules which passed through a 100-mesh sieve were
examined by the powder method.   The use of the block specimens,
which were obtained primarily for the purposes of microscopic exami-
nation, for X-ray examination was necessitated by the lack of other
corresponding material in a form better adapted for producing satis-
factory diffraction patterns.   The diffraction patterns of the blocks
were obtained by directing the primary X-ray beam at a small grazing
angle with the polished surface.   Some nitrided specimens of alumi-
num-molybdenum nitriding steels, kindly supplied by the Molybde-
num Corporation, were also analyzed.   Table 2 gives a summary of
the results.

It will be seen in Table 2 that all the specimens gave the hexagonal
close packed pattern except the iron specimens Nos. 13 and 39.   This
latter specimen, shown in Figures 18 (*c*) and 19, apparently does not
contain the intermediate nitride layer discussed in the microscopic
examination.   The fact that the hexagonal close-packed pattern ap-
peared in the iron specimens nitrided at 600° and 700° C. would indi-
cate that the hexagonal close-packed lines which were obtained can
not be due entirely to the outermost layer described in the micro-
scopic examination, since, as has been pointed out, this layer is de-
composed at these temperatures.   On the other hand, it has been
shown that the intermediate layer is stable at these and higher tem-
peratures.   The hexagonal close-packed pattern was also considered
as not being due to the inner one of the three nitride layers.   It ap-
peared more probable that this innermost layer has a face-centered
cubic lattice, since it shows a twinned structure and the presence of
this crystal structure was indicated in the X-ray spectrograms.   The
indications are, therefore, that the hexagonal close-packed pattern was
due to the intermediate one of the three nitride layers.

TABLE 2.—*Results of X-ray examination of various electrolytic iron and steel specimens nitrided at different temperatures*

[E. I.=Electrolytic iron.   Steel=Al-Mo nitriding steel (2.5 per cent Al; 0.85 per cent Mo; 0.25 per cent C.)]

Nitrided specimen			Nitriding treatment		Crystal structure of nitrided case, as determined by X rays [2]	Lattice parameter a_0[3] (A. U.)	Any face-centered cubic structure containing nitrogen present[4]
Laboratory No.[1]	Base material	Form—	°C.	Hours			
35	E. I.	Block	500	50	H. c. p.; B. c. c.	H. c. p.=2.72; B. c. c.= 2.86.	No.
77	do	do	500	50	H. c. p.	H. c. p.=2.72	Yes (1).
10	do	do	500	75	H. c. p. (and B. c. c.)	H. c. p.=2.71	No.
166 T	Steel	do	500	50	H. c. p.	do	Yes (1).
166 B	do	do	500	50	do	do	Do.
E 2	E. I.	Powder	540	50	do	H. c. p.=2.706±0.004	Do.
1000	do	do	540	50	do	H. c. p.=2.715±0.006	No.
7	do	do	550	2	H. c. p. (and B. c. c.)	H. c. p.=2.708±0.006	Do.
E 3	Steel	Sheet, 0.017 inch thick.	540	50	H. c. p.	H. c. p.=2.71	Yes (3).
37	E. I.	Block	600	25	B. c. c.; H. c. p.	B. c. c.=2.86; H. c. p= 2.73.	Yes (2).
168 T	Steel	do	600	25	H. c. p.	H. c. p.=2.71	Yes (3).
168 B	do	do	600	25	H. c. p.; B. c. c.	H. c. p.=2.71; B. c. c.= 2.86.	Yes (1).
13	E. I.	Powder	650	[5] ½	B. c. c. (and F. c. c. (N)).	B. c. c.=2.856 (F. c. c. (N)=3.777).	Yes. (2).
9	do	do	650	[6] 4	F. c. c. (N); H. c. p. (?).	F. c. c., (N)=3.780± 0.003.	Yes (5).
E 1	do	do	700	25	H. c. p.	H. c. p.=2.703±0.005	Yes (1).
39	do	Block	700	25	B. c. c.; F. c. c.	B. c. c.=2.86; F. c. c.= 3.60	Yes (2).
170 T	Steel	do	700	25	B. c. c.; F. c. c. (and H. c. p.).	B. c. c.=2.86; F. c. c.= 3.61.	Yes (1).
170 B	do	do	700	25	do	B. c. c.=2.85; F. c. c.= 3.61.	Yes (2).
E 4	do	Sheet, 0.017 inch thick.	700	25	H. c. p.; B. c. c.	H. c. p.=2.70; B. c. c.= 2.86.	Yes (2) or 3).

[1] The T and B after the three specimen numbers in this column stand for the top (decarburized before nitriding) and bottom (not decarburized) faces of the block specimens in question.   (See text.)

[2] H. c. p.=hexagonal close-packed (C=c_0/a_0=1.619); B. c. c.=body-centered cubic (a_0 for pure alpha iron=2.855 A.);F. c. c.=face-centered cubic (a_0 for pure gamma iron=3.60 A). In the cases where more than one crystal structure is present the more pronounced one is placed first. The structure reported in parentheses was present only to a small extent. F. c. c. (N) is face-centered cubic structure which is assumed to contain nitrogen in its space lattice, having a lattice parameter of about 3.80 A. U.

[3] With reference to the block and sheet specimens, the bands in the diffraction patterns were, as a rule, not sharply defined, more so for the interplanar spacings (d_h, k, l), of less than about 1.2 A. U. where the bands were broad and ill-defined and in some cases overlapped. After the usual corrections had been made for any length changes in the film, the deviations of the observed values from the theoretical values were plotted and corrections based on mean deviations were applied to the observed values. The results so obtained are reported only to the second decimal place. These difficulties did not apply to the powder specimens, so the results for these specimens are reported to the third decimal place.

[4] The figures given in parentheses are the number of bands observed which would fit in with a face-centered cubic structure having a lattice parameter of about 3.80 A. U. (3.789 A. U. according to Hägg) and could be clearly distinguished from the bands belonging to the hexagonal close-packed structure. It was noted that the theoretical values for several of the interplanar spacings in both the hexagonal close-packed and nitrogen-bearing face-centered cubic structures coincided. Since the series of hexagonal close-packed structure bands was more complete, the bands at the coinciding points were generally assumed to be due to this structure, unless the band in question appeared to be more intense than should be expected and in such cases the joint presence of the hexagonal close-packed and face-centered cubic bands was assumed. It was also noted that the band in the nitrogen-bearing face-centered cubic structure, due to interplanar spacing=approximately 1.90 A. U. possessed, in general, a strong intensity while the other observed bands were of weak or very weak intensity.

[5] Annealed in nitrogen after nitriding.

[6] Not annealed in nitrogen after nitriding.

In the discussion of the tentative iron-nitrogen diagram, which follows, the intermediate layer has been assigned the composition Fe_4N. There is, therefore, disagreement with the results reported by Hägg [17] who, in X-ray analyses of nitrided pure iron obtained by reducing powdered iron oxide with hydrogen and nitriding the iron

[17] Hägg, G., X-ray Studies on the Nitrides of Iron, Nature, 121, p. 826; 1928.

in the usual way, has given evidence indicating that the compound Fe_4N is face-centered cubic. Results somewhat similar to those obtained by Hägg were reported by other investigators,[18] but the X-ray data available at present appear to be insufficient to decide the matter definitely. It should be noted that no doubt is cast on the result obtained by Hägg that the compound Fe_2N is hexagonal close packed, and it may, perhaps, be suggested, in view of the very marked increase in the lattice parameter of the hexagonal close-packed patterns shown by him between the specimens of 6.1 and 11.3 per cent nitrogen content and likewise noted by Osawa and Iwaizumi, that the compounds Fe_4N and Fe_2N both have hexagonal close-packed patterns, the latter having the greater parameter.

It seems probable that the discrepancies in interpretation of the X-ray data are more apparent than real. Since Fry's diagram, which has probably been used as the basis for interpretation, does not recognize the presence of Fe_8N, the inner nitride layer is presumably taken by other workers as Fe_4N. If Fe_8N is admitted to be present, the discrepancies lie in the interpretation, not in the observations. Here again, as in the thermal analysis, interpretation is difficult because of the heterogeneous nature of the specimens and of inablility to isolate one layer at a time for study.

Reference was made above to the presence of a face-centered cubic lattice, to which the innermost layer described in the microscopic examination and given the composition Fe_8N, in the tentative iron-nitrogen diagram (fig. 20) was assigned. This face-centered cubic lattice appears to have a parameter of about 3.80 A. U., which is in good agreement with that reported by Hägg (3.789 A. U.). There was also found present in specimens 39, 170 T and 170 B a face-centered cubic lattice having a parameter of about 3.60 A. U. similar to that for pure gamma iron. It is suggested that this last face-centered cubic lattice may be due to rapidly cooled Braunite, which was present in some of the specimens and might be expected to give a face-centered cubic pattern analogous to that of austenite in quenched-high carbon steel. It might be mentioned that, in addition to the lines ascribed to the foregoing lattices, a number of lines possessing a very weak intensity in all cases were met with in a number of the diffraction patterns. Their identity has not yet been established.

VI. TENTATIVE IRON-NITROGEN DIAGRAM

The tentative diagram which has been drawn as a result of the study described above is given in Figure 20. It is to be emphasized, that this diagram is not an "equilibrium" diagram, as the term is generally used. The iron-nitrogen alloys are unstable and equilibrium conditions can not be determined without taking account of the pressure of nitrogen in the system and the activity of the nitrogen; that is, whether it is atomic or nascent or molecular. For instance, the temperature of the point D in the diagram, showing the stability limit of the compound Fe_4N, which was determined upon heating in ammonia gas, would undoubtedly be considerably lower in vacuum. It was even suspected during the work that since the arrests during the

[18] Osawa, G., and Iwaizumi, S., X-ray Investigation of Iron-Nitrogen Alloys, Sci. Repts., Tohoku Imperial Univ., (Sendai, Japan), 18, p. 79; 1929; Z. Krist, 69, p. 26; 1928; Chem. Abst. 23, p. 2408; 1929. Brill, R., The Crystal Lattice of Fe_4N., Z. Krist, 68, p. 379; 1928; Chem. Abst., 23, p. 2083; 1929.

thermal analyses were obtained on heating and not on cooling, most of the nitrogen being evolved during the run, they might be due entirely to decomposition and not to transformations between the solid constituents. Therefore a short series of tests were made. Seven samples of the nitrided granular electrolytic iron ranging in nitrogen content from 0.30 to 3.43 per cent were selected. The apparatus used consisted of an electric tube furnace through which was inserted a quartz tube, fitted to allow introduction of an alundum boat containing a weighed sample (2 g) and with connections to a vacuum pump and pressure gages. Temperature measurements were made by means of a portable potentiometer and 22 gage chromel-alumel thermocouple adjacent to the alundum boat containing the sample. Several blank runs were first made to determine the effect of heating upon the pressure variations of the evacuated system.

FIGURE 20.—*Tentative iron-nitrogen diagram*

Two pressure gages were used. A McLeod gage permitted pressure measurements up to 0.41 mm. Hg and an open end mercury manometer permitted readings of higher pressures.

One weighed sample of each nitrogen content was heated in the evacuated system for 15 minutes at 625° C. and another at 685° C., which are the temperatures corresponding approximately to the end of the two transformation ranges found by thermal analysis. A heating rate of approximately 7° C. per minute was maintained. Pressure readings were made at intervals of 50° C. and each 5 minutes of the 15 minutes at temperature. The specimens were cooled in the sealed system and then analyzed for residual nitrogen. Figure 21 shows the pressure variations during heating of some of the samples. The first noticeable increase in pressure due to evolution of gas occurred at 200° to 250° C. and another increase in pressure at 400° to 450° C., the magnitude of this latter increase being governed by the initial nitrogen content. Samples of higher nitrogen content gave the

greatest increase. As the temperature was raised to 625° or 685° C., the pressure increased rapidly. Considerably higher pressures were obtained upon heating to 685° C. than by heating to 625° C. All samples showed a loss of weight after heating and in every case the samples heated to 685° C. showed a greater loss than the corresponding sample heated to 625° C. Chemical analysis of the samples for residual nitrogen confirmed the weight losses. Since evolution of gas began well below the temperatures of the transformation ranges and the pressures increased continuously and not in two sudden stages, it seems that the heat effects at the two transformation temperatures can not be attributed solely to decomposition. They really represent phase changes.

That the thermal arrests represented transformations between the solid constituents was, of course, confirmed by the microscopic examination. It may also be mentioned that, since the nitrided specimens were prepared by diffusion and not by melting, the composition gradients are not smooth but occur in steps between adjacent nitrided layers. As called for by the principles underlying the construction of equilibrium diagrams, a duplex field marked $Fe_6N + Fe_4N$ has been indicated in the diagram; actually there were no signs of such a field in the microstructure. The compounds were found to occur directly adjacent to each other. A similar result obtained in the diffusion of melted zinc into solid copper at 450° C. has been described by Hudson.[19]

The outer, intermediate, and inner layers noted in the microstructure have been designated as the compounds Fe_2N, Fe_4N, and Fe_6N, respectively. (Fig. 20.) No chemical analyses of the compositions of the individual nitride layers were made, as they could not be sharply separated, and stoichiometric relations such as those of Noyes and Smith,[20] who reported Fe_2N, Fe_4N, Fe_6N, and Fe_8N as possible compounds, were used as the principal guide for setting the compositions of the layers. This construction is a modification of Fry's diagram, which showed only two layers. The intermediate layer described in the microscopic examination is the one which corresponds in microstructure to Fry's Nitride I, and it should be noted Fry designated this layer as Fe_2N whereas in this diagram it is designated Fe_4N.

This departure from Fry's diagram appears to be justified by the fact that the outermost layer was not noted by Fry and because the construction shown fits in with the thermal analysis data obtained by Sawyer and in this work. Moreover, on the grounds of Fry's own observations it would appear better to designate his Nitride I (corresponding with the intermediate layer described in this study) as Fe_4N, instead of Fe_2N. The layer, Nitride I, in Fry's micrographs is shown to be stable at the nitriding temperature of 680° C, which he used, whereas his diagram indicates the compound Fe_2N to be unstable at comparatively low temperatures.

Since the outermost layer, designated as Fe_2N, has a 2-phase eutectoid-like structure it may be considered as a eutectoid between the compounds Fe_4N and Fe_2N, the eutectoid transformation probably occurring below 425° C., as indicated by Figure 10 (f) in which the

[19] Hudson, O. F., The Critical Point at 460° C. in Zinc Copper Alloys, J. Inst. Metals, **12**, No. 2, p. 89; 1914.
[20] Noyes, A. A., and Smith, L. B., The Dissociation Pressure of Iron-Nitrides, J. Am. Chem. Soc., **43**, No. 1, p, 475; 1921,
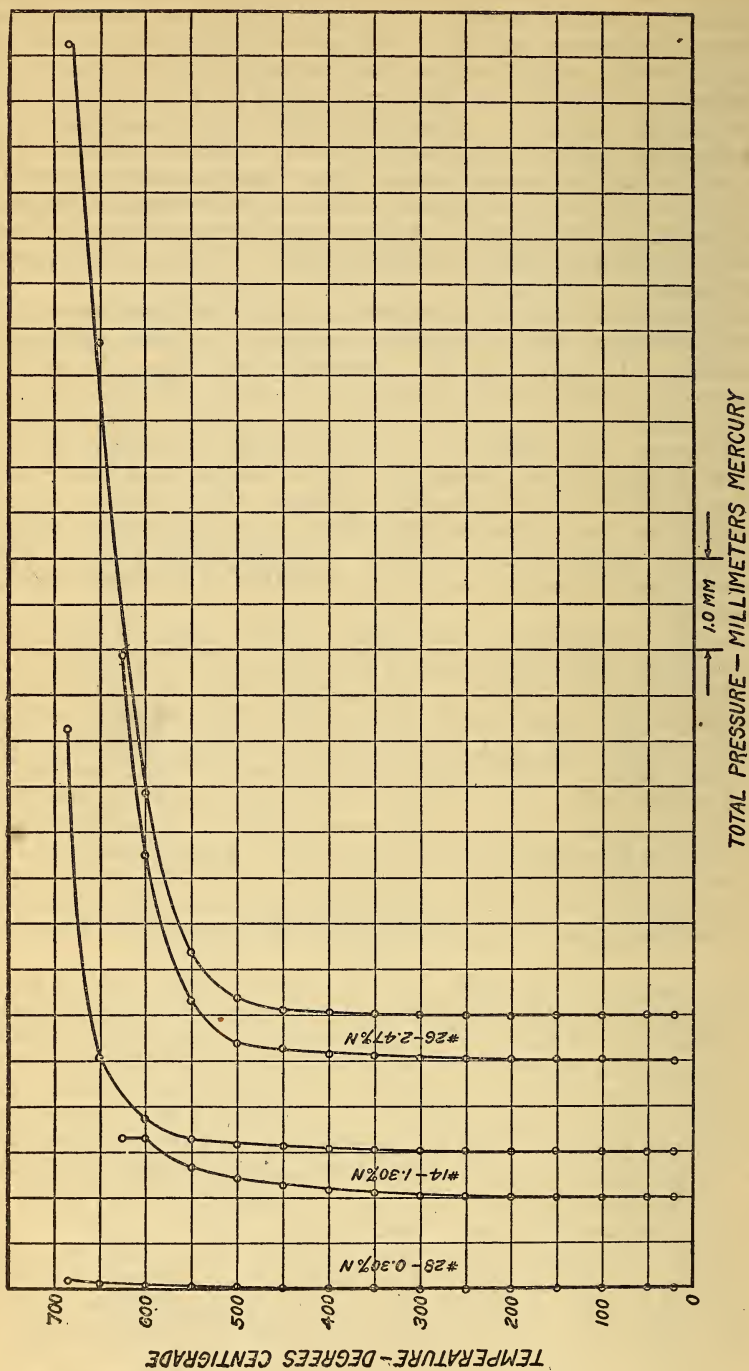
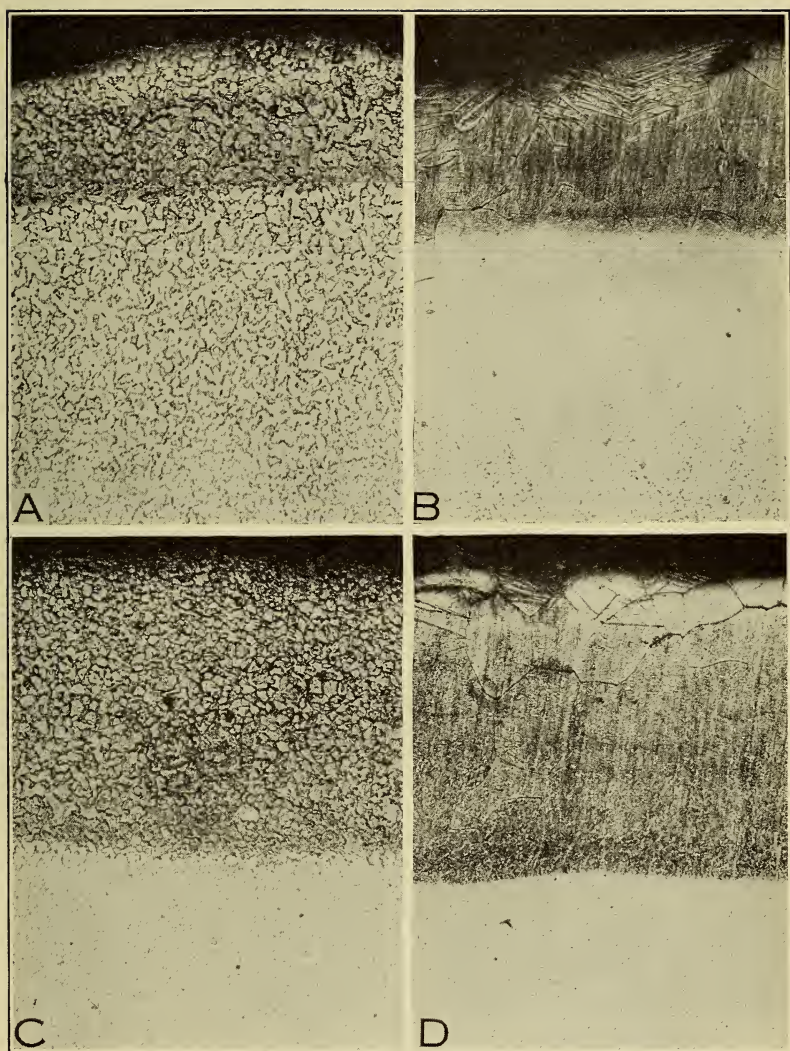FIGURE 21.—*Change of pressure during the heating of some of the samples for thermal analysis*

FIGURE 22.—*Nitrided layers in special aluminum-molybdenum nitriding steels,* × *100*

a, Nitrided 50 hours at 500° C. Note that the original structure of the steel can still be discerned in the nitrided layer. There is only one layer. No nitride needles were detected in the cores of any of the nitrided steels; *b,* same as specimen *a,* but at edge decarburized before nitriding. Note the coarse crystal structure and the wide slip lines or twins near the surface; *c,* nitrided 25 hours at 600° C. The nitrided layer is deeper than in *a* or *b* because of the higher temperature of nitriding; *d,* same as specimen *c,* but at decarburized edge. Slip lines are present in the coarse crystals, but they are not so numerous as in *b,* nitrided at the lower temperature.
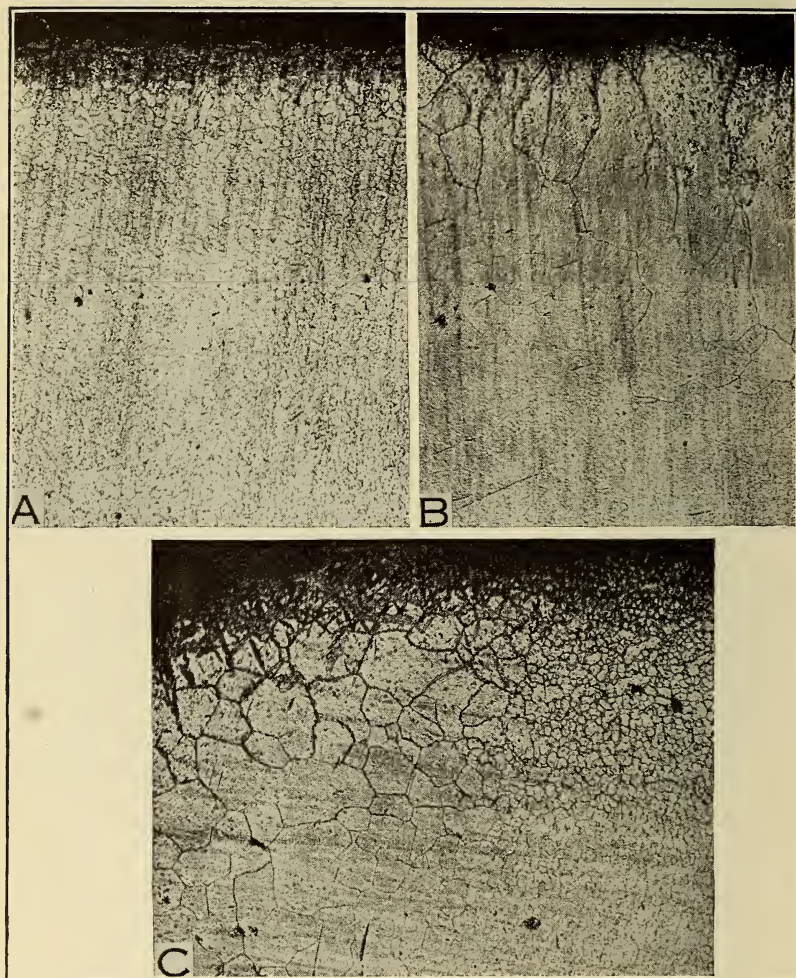
FIGURE 23.—*Structure of steel specimens nitrided 25 hours at 700° C.,* × *100*

a, Fine grain at undecarburized edge of block; *b,* coarse grain at decarburized edge of block. At this high nitriding temperature, however, no slip lines appeared; *c,* juncture of decarburized and undecarburized edge. Note the intergranular darker constituent which appears at this nitriding temperature.
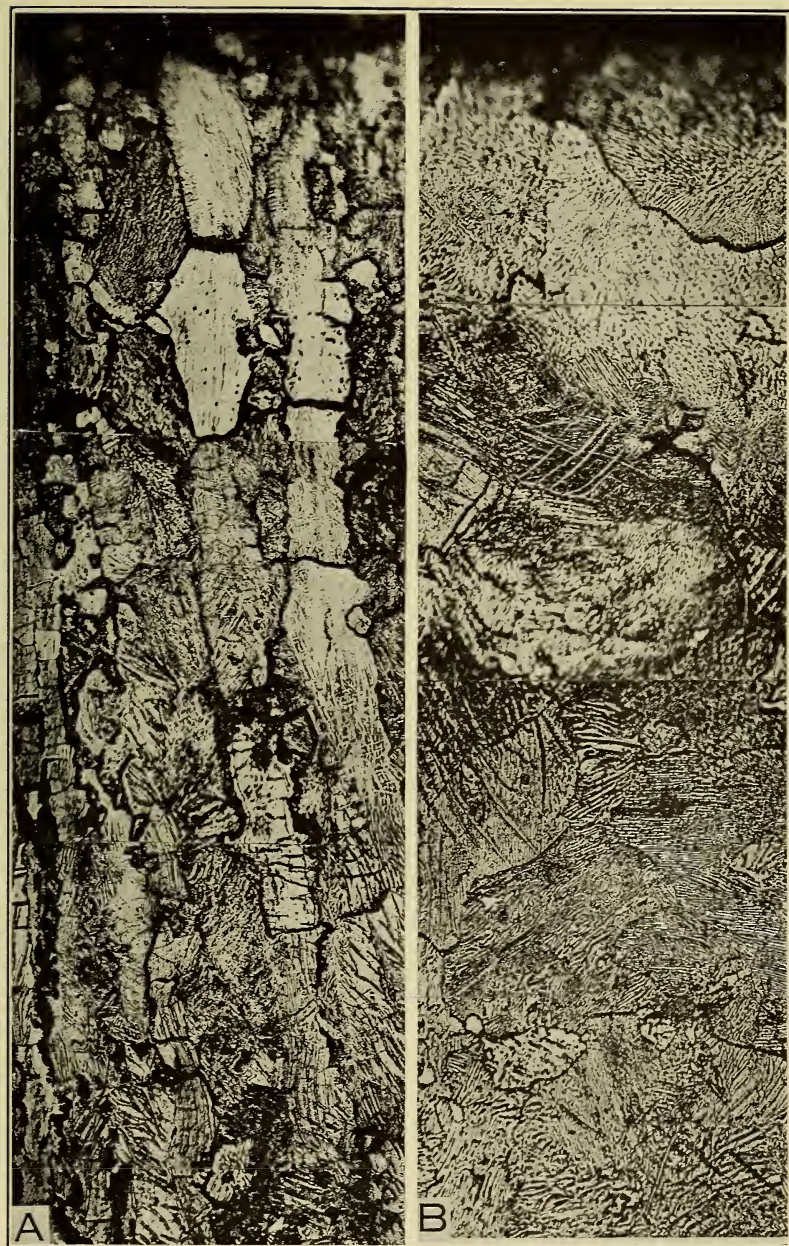
FIGURE 24.—*Slip lines in nitrided layers,* × *500*

Nitrided 25 hours at 540° C. *a*, Note number of slip or check lines toward the interior. These slip lines were found to be present very close to the core; *b*, this specimen contained no molybdenum.
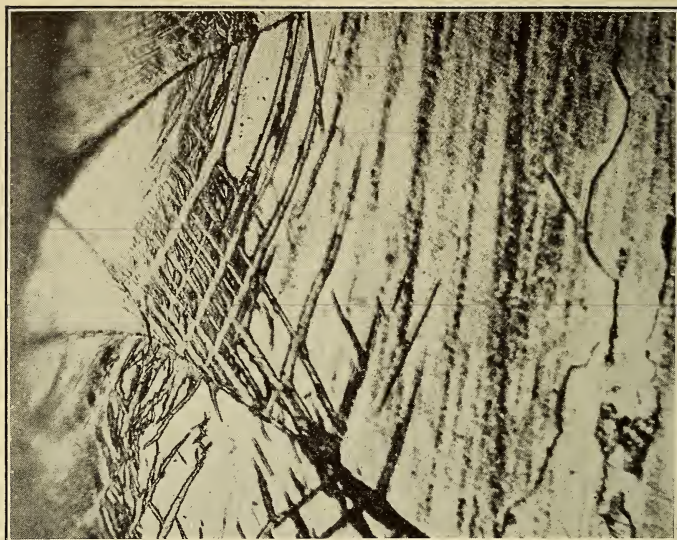
FIGURE 25.—*Slightly rounded twins and slip lines in coarse-grained nitrided layer,* × *500*

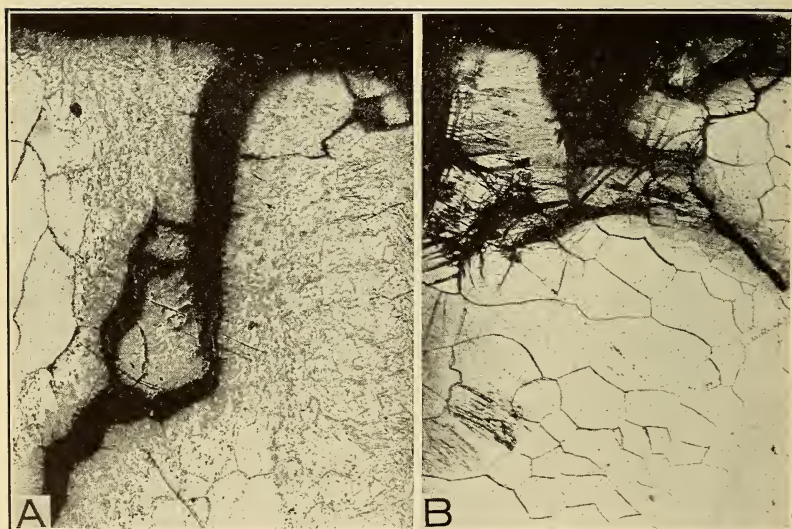Nitrided 25 hours at 540° C. at the decarburized edge of the block.

FIGURE 26.—*Fissures and darker etching constituent in nitrided specimen heated to 725° C. in NH₃,* ×*500*

a, Nitrided 25 hours at 600° C., then heated one hour in NH₃ at 725° C.; b, nitrided 25 hours at 700° C., then heated one hour in NH₃ at 725° C.

eutectoid structure was obtained by nitriding at that temperature. There was, however, no indication of such a eutectoid shown by the thermal analysis.

From the results of Noyes and Smith the innermost layer might have been designated either Fe_6N or Fe_8N, since they consider both are possible. However, a vertical line corresponding to the compound Fe_8N of approximately 3 per cent nitrogen content meets the upper horizontal at the point C, in which case the lines BC, CD, and CE, would all meet the vertical line of the compound at the point C. This does not appear at all probable and the compound Fe_6N was chosen to designate the innermost layer.

The reasons for modifying Fry's and Sawyer's diagrams by the peritectoid horizontal CE have already been given. For the solid solubility line MG Fry's diagram has been followed, although it appears that the solid solubility at the eutectoid temperature, namely, the point G, is not very definitely established. The temperatures for the lower eutectoid horizontal GK, 600° C., and the upper peritectoid horizontal CE, 675° C., are taken as rounded figures, from the results of Sawyer, Fry, and those obtained in this study.

Fry's temperature scale has been regarded as about 10° too low [21] and this was considered in setting the temperature of the eutectoid horizontal at 600° C. It will be noted that the point C at 3 per cent nitrogen content, at which composition the upper horizontal begins, is at a considerably higher nitrogen content than the composition at which the upper horizontal first appeared in the thermal analyses. As shown in Figure 5 this was at 1.25 per cent. As has already been stated, however, the nitrogen content in the nitrided layers in this composition range appeared to be about three times the average nitrogen content. The location of the point C for the beginning of the upper horizontal is therefore in fair agreement with the thermal analysis results.

Since in the present work the peritectoid transformation was completed below 675° C. in a large majority of the cases and always began below 660° C., it is possible that the rounded value of 675° C. is a trifle high.

VII. OBSERVATIONS ON THE STRUCTURE OF NITRIDING STEELS

The aluminum-molybdenum nitriding steels mentioned in connection with the X-ray analyses were also examined under the microscope. They contained 2.5 per cent aluminum, 0.85 per cent molybdenum, and carbon 0.25, except one specimen (see fig. 24) which contained 0.50 per cent carbon and no molybdenum. As may be seen in Figure 22, the steel specimens, unlike the nitrided iron specimens, showed only one nitrided layer, which was yellowish in color darkened brown by etching with picric acid. The original structure of the steels was not changed to any degree by the nitriding and may be discerned in the nitrided layer. (Fig. 22 (a)). Even in specimens of nitrided sheet of this material, the original worked structure still remained, the nitriding being evident in the microstructure only by the yellowish tinge of the nitrided layer. In none of the steel speci-

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[21] Bramley, A., and Haywood, F. W., Determination of the Iron-Iron-Nitride Eutectoid, Carnegie Schol. Mem., **77,** p. 76; 1928.

mens, including those which were heated to 725° C. was there any evidence of a eutectoid layer corresponding to Braunite. The steel specimens also differed from the nitrided iron specimens in that in the former no nitride needles were present in the case, which is, of course, important on account of the embrittling effect of the nitride needles. The absence of nitride needles in the nitriding steels is most readily explained by the fact that only one nitrided layer is present. As was pointed out by Fry and observed in the microscopic examination of the nitrided iron specimens, the familiar nitride needles are evidently due to the innermost layer, which is not formed in these special alloy steels used for commercial nitriding.

The steel specimens were nitrided at 500°, 600°, and 700° C., respectively. Those nitrided at the lower temperatures appeared to be more brittle than those nitrided at the higher temperatures. The specimens were in the form of blocks, one edge of which had been decarburized before nitriding. In these decarburized edges of the specimen the grain size was comparatively large and in the specimens nitrided at the lower temperatures these large-grained areas showed profuse twinning and slip line formation, as shown in Figures 22 (b) and (d) and in Figure 25. In the specimens nitrided at the higher temperatures, however, the slip lines did not appear to any marked degree, as shown in Figure 23 (b) and (c). Moreover, in the fine-grained areas slip lines or twins were practically absent even in those nitrided at the lower temperatures, as shown in Figures 22 (a) and (c). Since the slip lines which formed in the large grained areas are evidently an indication of brittleness it is apparent that the presence of surface decarburization in nitriding steel should be guarded against. Due to the extreme hardness of the nitrided layer, particularly at the surface, it would be expected to be very brittle. It was observed, as shown in Figure 24, in specimens in which the nitrided layer was tapered off gradually by grinding, that large numbers of slip or check lines were also present very close to the core. This is especially apparent in the specimen shown in Figure 24 (a).

Two of the specimens were heated to 725° C. in ammonia for one hour. After this treatment, as shown in Figure 26, the nitrided layers gave evidence of the presence of another constituent which was etched slightly darker than the matrix by sodium picrate. Fissuring of a type probably similar to that described by Vanick, Sveshnikoff, and Thompson [22] also occurred. These authors concluded that fissuring was generally preceded by decarburization.

It was observed that the fissuring of these specimens was also much more pronounced in the edges of the specimens which had become decarburized before nitriding.

In the X-ray analyses summarized in Table 2 the steel specimens nitrided at 700° C. showed more than one crystal pattern, whereas those nitrided at the lower temperatures showed only one pattern, namely, the hexagonal close packed. Under the microscope also, as shown in Figure 23, another constituent was noticed, present as a grain boundary network. This result is of some interest, since nitrided articles have been suggested for use at comparatively high temperatures, and it would appear necessary to obtain assurance of the stability of the different nitriding steels at these temperatures.

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[22] Vanick, J. S., Sveshnikoff, W. W., and Thompson, J. G., Deterioration of Steel in the Synthesis of Ammonia, B. S., Tech. Paper No. 361.

VIII. SUMMARY

1. In a study of the iron-nitrogen system, thermal analyses, microscopic examinations, and X-ray analyses were made of nitrided electrolytic iron specimens. From the data obtained and, with the diagrams of Sawyer and Fry as a basis, a modified iron-nitrogen constitution diagram has been tentatively drawn.

2. The thermal analysis data, in general, confirm those of Sawyer which indicated that there are two temperature horizontals on the high nitrogen side of the diagram, but the microscopic examination indicated that the upper horizontal represented a peritectoid reaction, and not a eutectoid transformation as Sawyer supposed.

3. Three iron nitride layers were observed, whereas Fry in his pioneer work and Murakami in his recent work noted two. The outer, intermediate, and inner layers have been designated as Fe_2N, Fe_4N, and Fe_6N, respectively.

4. In X-ray analyses a hexagonal close-packed pattern and indications of a face-centered cubic pattern were obtained. According to the microstructure of the layers it appeared probable that the face-centered cubic lattice was due to the inner layer Fe_6N and the hexagonal close-packed pattern to the intermediate layer Fe_4N; this is not in agreement with the interpretation of X-ray data by Hägg, Osawa, and other investigators who ascribe the face-centered cubic lines to Fe_4N. The data available at present do not appear to be sufficient to definitely decide the matter.

5. Observations on several nitrided specimens of aluminum molybdenum nitriding steel were also made. Those nitrided at the usual nitriding temperatures contained only one layer and showed a hexagonal close-packed pattern.